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2. Mineralogy – Petrology – Geochemistry





2. Mineralogy – Petrology – Geochemistry

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C-O-H solubility under reduced conditions in a haplobasaltic liquid: implications for Mars degassing

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Oxygen fugacity (fO_2) may have a critical influence on the solubility of volatiles in silicate liquids, which in turn influences fluxes of volatiles from planetary interiors to their atmospheres. Carbon dissolves in oxidized basic melts as carbonate but under reduced conditions is limited by precipitation as graphite or diamond. At conditions where melt is in equilibrium with Fe alloy, the carbonate solubility will not exceed few ppm (Hirschmann & Withers, 2009), limiting volcanogenic transport of C to the atmosphere. Therefore, dissolved C-H species may dominate C solubility and transport at low fO_2 (Mysen et al., 2009; Kadik et al., 2006, 2010)

In this study, we investigated the solubility of C-O-H fluid in a haplobasaltic melt ($Di_{40}An_{42}Ab_{18}$), adding C as $Si_5C_{12}H_{36}+H_2O$ to produce $SiO_2+CH_4+H_2$ and H_2O (Mysen et al., 2009). Experiments were performed using endloaded piston cylinder apparata at pressure of 0.7, 1.5, 2.0 and 3.0 GPa, and at fix temperature of 1400°C. The fO_2 was buffered using a double Ptcapsule technique, where the external buffer (e.b.) fixed the fH_2 by transport across a H-permeable Pt barrier, and the internal buffer (i.b.) set the fO_2 of the silicate charge. In this study we used three buffer combinations: 1) e.b. with Fe-FeO-Fe₃C-H₂O, or Mo-MoO₂-Mo₂C-H₂O and i.b. powder graphite; 2) e.b. with Fe-FeO-H₂O and i.b. Si⁰, and 3) the more oxidized one using as e.b. Ni-NiO-H₃O and i.b. Si⁰.

After quench we checked the external capsule for water by piercing the Pt walls and afterward the capsule was opened using a Mo-wire along the capsule axis. At first we examined the capsules for the bufferphases and afterwards we examined resulting glasses, the bubbles and the solid phases by optical and SEM microscopy to establish equilibrium coexistence of the melt with a fluid phase and verified glass compositions with EMPA. Dissolved volatile species were identified by microRaman spectroscopy and OH and C concentrations were quantified by FTIR and SIMS, respectively.

Results show that C dissolves as methane together with OH, H_2O and H_2 in equilibrium with a volatile phase composed chiefly of CH_4 and H_2 . At IW to IW-2 (buffer 1) the dissolved C increases linearly with pressure from 70 ppm at 0.7 GPa to 360 ppm at 3.0 GPa (Figure 1), and similar increase with pressure are found using the Fe-FeO- H_2O buffer (2; IW0 to -3). Hydrogen dissolved in the melt as OH, H_2O and H_2 speciation. Preliminary SIMS and FTIR results indicate large solubility of H_2 molecules in the quenched melt, showing a difference as a function of the hydrogen fugacity imposed by the different buffers, and the total water of the starting material. The results indicate that hydrogen dissolves almost equally as H_2 and total water (OH and H_2O).

Carbon dissolves as methane at reduced conditions, therefore methane is the dominant carbon species at low oxygen fugacity, which could be outgassed from reduced planetary mantles. Example of today and hystorical Mars atmosphere could be partially explained by large C emission into the atmosphere trough outgassing of CH₄ rich basalts.

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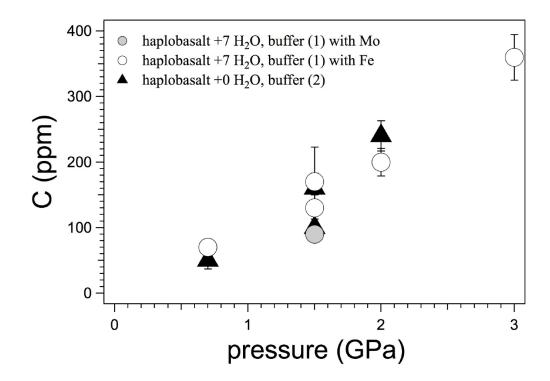


Figure 1. Carbon solubility in ppm with increasing pressure for the haplobasalt synthesised using the buffer (1), Fe-FeO-Fe $_3$ C-H $_2$ O (white cirle), or Mo-MoO $_2$ -Mo $_2$ C-H $_2$ O (grey circles) as external buffer and graphite internal buffer, and buffer (2) with Fe-FeO-H $_2$ O as external buffer and Si o as internal buffer (black triangles).

2.2 Some consequences of mechanical and diffusional closure in garnets

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Partial molar volumes of components in solutions differ typically for several percent. As a consequence, diffusion of components will result in changes in volume. Such volume changes are easily accommodated in liquids, resulting in volume increase in one part of the diffusion zone, and volume decrease in the other. In crystals such volume changes result in stress. In the extreme case, in which a mineral behaves perfectly elastic (e.g. rigid), such volume changes result in large stresses. For example, assuming a garnet crystal to be accommodating a volume change accompanying diffusional mass transfer of 0.1 X (grossular) in a pyrope solid solution requires a local 15Kb pressure change to accommodate in an elastic fashion the induced volume change. Hence minute inclusions in garnets could report pressures, which are significantly higher (or lower) than the ambient pressure. Stress differences will of course be relaxed by the plastic behavior of minerals. If such Maxwell relaxation is faster than diffusion, the mineral will approach the diffusion behavior of a liquid. Hence the crucial question is if there is experimental or natural evidence for the rigid behavior of minerals?

Recently published experiments by Vielzeuf & Saul (2010) indicate that mechanical relaxation is slower than diffusion. In these experiments they used an overgrowth methodology to obtain coherent garnet crystal with a step discontinuity between seed and overgrowth. We calculated the molar volume for each part, seed and overgrowth, and found that the molar volume of the garnet remained constant for each zone in their experiments at 1150°C and 1200°C, at 1250°C, some mechanical relaxation seems to occur. This indicates that diffusion is faster than mechanical relaxation at lower temperatures. Hence mechanical closure of the system occurs at higher temperatures than diffusional closure, for these garnets. Following up in natural systems, we investigated the diffusion haloes surrounding coesite inclusions in garnets from Dora Maira. The observed Ca-depletion zones surrounding the inclusions can be interpreted to result from the pressure exerted from the inclusion onto the surrounding garnet. Here garnet volume did decrease due to pressure "pushing away" the

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largest partial molar volume component, grossular. Hence, diffusion can be initiated by pressure gradients in minerals. The above observations are consistent with a Helmholtz approach for the chemical potential. We have also developed a simple model coupling mechanics with diffusion, to illustrate the difference of liquid-like diffusion and solid-like diffusion.

Finally, these observations lead us to speculate that micro-inclusions, such as diamonds, in garnets might indicate P conditions which were never experienced by the rock matrix as a whole. Similarly, using diffusion coefficients to analyze thermal cooling histories might result in erroneous time estimates, since pressure gradients – produced by diffusion or also prograde pressure during growth – will influence the diffusion behavior, if the concept of mechanical closure is neglected.

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2.3

Petrological insights into shifts in eruptive styles at Volcán Llaima (Chile)

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Tephra and lava pairs from two summit eruptions (2008 and 1957 A.D.) and a flank fissure eruption (~1850 A.D.) are compared in terms of textures, phenocryst contents, and mineral zoning patterns in order to shed light on processes responsible for the shifts in eruption style during typical eruptive episodes at Volcán Llaima (Andean Southern Volcanic Zone, Chile). The mineralogy and whole-rock compositions of tephra and lavas are similar within eruptive episodes, suggesting a common magma reservoir for Strombolian paroxysms and lava effusion. The zoning profiles and textures of plagioclase record successive and discrete intrusions of volatile-rich mafic magma accompanied by mixing of these recharge magmas with the resident basaltic-andesitic crystal mushes that are commonly present at shallow levels in the Llaima system. The shallow magma reservoir of Volcán Llaima resembles that of Stromboli volcano (Italy) in that it contains a highly viscous crystal-rich magma, which is frequently refilled by low viscosity, nearly aphyric, and volatile-rich magma. Each recharge event destabilizes the plagioclase in equilibrium with the resident crystal mush and stabilizes relatively An-rich plagioclase, as is recorded by the numerous resorption zones. Lavas typically have ~15-20 vol% more phenocrysts than the tephra. Differences in plagioclase and olivine textures and zoning, combined with different phenocryst contents, indicate that a greater volume fraction of recharge magma is present in the explosively erupted magma than in the effusively erupted magma. We propose that Strombolian paroxysms at Volcán Llaima are triggered by interactions with large volume fractions of recharge magma, which decrease the bulk viscosity and increase the volatile contents of erupted magmas, favouring large expansion velocities required for the fragmentation of basaltic-andesite. Lava effusion ensues from reduced interactions with the recharge magma, after it has partially degassed and crystallized, thereby impeding rapid ascent. This process could be operating at other steady-state basaltic volcanoes, such as Stromboli or Villarica (Chile) volcanoes, wherein shallow reservoirs are periodically refilled by fresh, volatile-rich magmas.

Polymetallic mineralization in the Laki mining district Southern Bulgaria: Paragenesis and fluid evolution

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The Laki mining district in southern Bulgaria is home to a number of Pb-Zn-Ag-(Cu) deposits. The district lies within the Central Rhodopian Dome (CRD), regarded as one of the most internal Alpine zones, related to the Aegean subduction system (Marchev et al., 2005). The CRD hosts several mining districts located in Madan, Laki, Ardino, Davidkovo and Enyovche, which have been dated as Oligocene (Kaiser et al., 2004). These districts show similar ore-body types of low- to intermediate-sulfidation mineralization, typically occurring in veins and metasomatic bodies. Four of the mining districts of the CRD are in close vicinity to the Middle Rhodopian detachment fault (Ivanov et al., 2000), which is cross-cut by rhyolite dykes and ore veins. The Laki district is made up of four linear ore-bearing NNE-trending faults, which also cross-cut subvolcanic bodies associated with the Borovitsa caldera.

The focus of this study centres on the Djurkovo deposit, in the Laki district. Mineralization is concentrated in two main veins, named West 2 and the Eastern Apopyhsis, hosted in gneisses and marbles of the Asenitsa Unit (Ivanov et al., 2000). Both veins trend NNE-SSW, dip steeply towards the NW and reach a thickness of up to 2 meters. Average grades of West 2 are 3.76% Pb, 1.40% Zn, 0.29% Cu and 49 g /t Ag, while the Eastern Apophysis vein has grades of 5.29% Pb, 0.91% Zn, 0.46% Cu and 128 g/t Ag. Metasomatic bodies occur up to 140m from where veins cross-cut marble horizons. Ore grades from the metabodies vary from 2.9-3.6% Pb, 3.0-4.2% Zn, 0.2% Cu and 30 g/t Ag. All ore-bodies are cross-cut and displaced to various degrees by E-W normal faults, related to the late exhumation of the district. Detailed petrography and chemical analysis of ore and gangue minerals, is combined with fluid inclusion microthermometry, on samples collected from a vertical interval of 200m, in order to fully understand the P-T-X evolution of the ore-forming fluids.

The paragenetic sequence of the Djurkovo deposit can be simplified into three main stages for the veins: an early quartz-pyrite stage; a polymetallic stage; a late quartz carbonate stage, while the metasomatic bodies contain a prograde skarn stage caused by fluid-rock interaction. Chlorite occurs throughout all of these stages, as well as being one of the main alteration minerals of the host rocks, along with adularia, epidote and carbonate. This abundance and the tendency for chlorites to vary in composition due to variations in fluid conditions (temperature, chemistry, etc.) makes them useful indicators for the evolution of fluids at Djurkovo. Chlorite composition is represented by $(Mg,Fe^{2+},Fe^{3+},Mn,Al)^{VI}_{6}[(Si,Al)^{IV}_{4}O_{10}]$ $(OH)_{8}$, with cation substitution occurring in both octahedral and tetrahedral sites.

Careful petrography was carried out, followed by electron microprobe analysis of chlorites, from both veins and mesasomatic bodies, to determine the compositional variation through time. Chemically the chlorites occur as tri-octahedral chamosites and clinochlores. Cation substitution observed occurs as $Si^{4+}Mg^{2+} \leftrightarrow {}^{IV}Al^{VI}Al$; $Fe^{2+} \leftrightarrow Mg^{2+}$; $Fe^{2+} \leftrightarrow Mn^{2+}$; $Fe^{3+} \leftrightarrow Al^{IV}$; with anion substitution occurring in some areas as $OH^- \leftrightarrow F^-$.

Formation temperatures of the chlorites were calculated using the Cathelineau (1988) equation, based on the Al^{IV} content in the tetrahedral site, range from 390°C to 270°C in the veins and 390°C to 125°C within the metabodies. Variations in Fe^{3+}/Fe^{2+} ratio appear to be inversely correlated to the temperature of formation. Elevated Fe^{3+}/Fe^{2+} values may represent an increase in the oxidation state of the fluids through time, as well as a deficiency in aluminium required to balance the negative charge of the tetrahedral layer.

Electron microprobe analysis of sulfides has revealed that both galena and pyrite show varying compositions through time. The galena contains variable amounts of Bi and Ag. Observed substitutions within galena occur as $2Pb \ \mathbb{Z} \ Bi^{3+}+Ag^+$. Bonev (2007) observed that in the Madan district galena with elevated amounts of Bi are associated with high temperatures, while lower temperature galena does not show a presence of Bi. This study suggests that elevated values of (Bi+Ag) are present in the vein ore bodies for samples analyzed, while metabodies from the same locality exhibit up to 10 times lower (Bi+Ag). Maximum contents of Bi and Ag in the veins are 5 and 2.5 wt.% respectively. No significant difference is noted in the (Bi+Ag)/Pb between the two major veins. Metabodies show maximum values for Bi and Ag of 0.39 and 0.04 wt.% respectively. Minor quantities of Pb-Bi-Ag-Cu sulfosalt and aikinite, are present in some areas. Aikinites are present as a solid solution in the Bi_2S_3 -Cu₂S-Pb₂S₂ system and can be classified as hammarites.

X-ray mapping of pyrite grains indicate oscillatory zoning caused by As, and Co attributed to a minor amount of zonation. Arsenic rich zones are limited to the earlier generation of pyrite, while Co tends to form later.

Further work on fluid inclusions in both transparent and opaque minerals, including LA-ICP-MS trace element analysis provide insight to the fluid evolution in the Djurkovo deposit, with possible implications for the evolution of the Oligocene base metal deposits of the Rhodopian Dome.

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2.5

Probing solid-solution formation via magnetic freezing dynamics

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The hemo-ilmenite solid solution (x)FeTiO₃ - (1-x)Fe₂O₃ is an important magnetism carrier in the Earth's crust. The system exhibits ferrimagnetism for compositions 0.5 < x < 0.95 and antiferromagnetism for 0.0 < x < 0.5, with an ordering temperature, that depends on the composition (Charilaou et al. 2011a). For compositions 0.6 < x < 0.95, it exhibits a spin-glass-like freezing at low temperature (T < 50 K) due to Fe(II) - Fe(III) interaction-induced frustration (Charilaou et al. 2011b). The characteristics of the freezing can reveal the intrinsic mechanisms of magnetic interactions, which strongly depend on the crystalline homogeneity and cation order. Therefore, using well-defined synthetic hemo-ilmenites as comparison permits a deeper understanding of the physical properties of naturally formed solid solutions. In this report we compare data for synthetic and natural hemo-ilmenite solid solutions with composition 80% and 83% ilmenite, respectively. The comparison is based on quantitative analysis of the freezing dynamics using ac susceptibility (Charilaou et al. 2011c). From the experimental data we extract the effective relaxation times of the magnetic structure which reveal that naturally occurring solid solutions only exhibit short-range order, which clearly indicates the cooling rate effects on the formation of solid solutions.

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Evidence for trace element mobilisation in garnet-phengite eclogitic veins along a metabasite-micaschist contact during HP conditions: an example from the Ile de Groix, France

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A complex vein network in metabasites and micaschists on the Ile de Groix is thought to result from diverse fluid-rock interactions during both prograde and retrograde metamorphism (El Korh et al., 2011). Rare eclogitic HP–LT veins have a phe-grt-ep-rt-ilm-qtz-ab-pg-ap assemblage dominated by garnet and phengite. They are hosted in eclogite facies metabasites composed of grt-agr/jd-barr-gln-rt-ep-qtz-ab-chl-ilm-mt (peak conditions: ~ 2.0 GPa; 450–550°C) that are in contact with metapelites. Metasomatism of the host eclogite is evidenced by its high Na $_2$ O content (6.0 wt%) and high proportion of Na-rich minerals (agr-jd and gln), and by its low MgO content (1.8 wt%).

Major and trace element compositions of minerals and the petrology support a multi-stage vein formation at HP conditions. During the first stage of vein formation, garnet cores, enriched in MREE and HREE, formed in equilibrium with LREE-, Th- and U-rich epidote I, and Ti- and Ta-rich rutile. During the second stage of vein formation, LILE-rich phengite and chloritoid have grown synchronously with garnet rims, HREE depleted compared to their cores, as well as with epidote II, with a flat REE pattern, and albite. Ilmenite formed after rutile and incorporated small amounts of Nb and Ta. Phengite is related to a strong LILE enrichment of the vein. Paragonite formed during the last stage of vein formation as a result of a reaction between albite and phengite. Paragonite consequently inherited a part of the LILE from phengite. A few inclusions of paragonite were detected in garnet rims, supporting paragonite growth during late garnet formation. The HREE-rich and LREE-depleted epidote III occurs in equilibrium with paragonite.

Eclogitic garnet-phengite veins hosted by eclogite facies metabasites along the contact metapelite-metabasalt, provide evidence of cumulate fluid flow. The strong HREE and HFSE enrichments in vein garnet and rutile, as well as the LREE enrichment in epidote, result from a mass transfer from the host metabasite involving an internally derived fluid during the first stage of vein formation. The fluid was able to mobilise the REE and HFSE on a small scale, but precipitation thereof within the vein minerals.

During the second stage of vein formation, the fluid responsible for the formation of phengite, chloritoid, ilmenite and garnet rims contained LILE and REE. Addition of an external fluid is necessary to explain the LILE enrichment. Phengite content, reaching 20–25% in the vein, is too high to originate from the host metabasites, which only contain 3–5% phengite, This fluid could originate from the neighbouring micaschists. The LILE composition of phengite is intermediate between the LILE compositions of phengite in metabasites and micaschists, suggesting an input of a pelite-derived fluid in addition to the internally derived fluid from the metabasic host rock. This fluid is able to transport LILE at least on a meter scale. Growth of paragonite and epidote III is related to re-equilibration during the last stage of vein formation.

The fluid $d^{18}O$ values of 10.8–12.1‰ (relative to VSMOW) calculated in equilibrium with garnet and phengite from the vein corresponds to an average between values estimated to be in equilibrium with massive metabasite hosts (8.9–9.6‰) and nearby micaschists (11.3–12.1‰). The fluid isotopic composition does not allow the internal and external fluid inputs to be quantified as the two sources (host metabasites and near-by metapelites) provide isotopic values that are relatively close (\pm 3‰).

Eclogitic garnet-phengite veins along metabasite-metapelite contacts provide evidence of local fluid migration, sourced in the surrounding rocks. Vein-forming fluids are responsible for significant mass transfer from source rocks to veins. The veins contain minerals with enrichments of HREE and HFSE, generally considered as immobile, but transported on a small scale from the host metabasites and host metapelites to the veins. HREE and HFSE mobility requires intense fluid-rock interactions, enhanced by fracturation along the foliation plane, and necessitates the destabilisation of the prograde HFSE-and HREE-rich minerals titanite and garnet of the vein-hosting rocks. The transport of HREE and HFSE is allowed through F and dissolved Na-Al-Si polymers in the fluid as complex formers (Haas et al., 2005; Antignano & Manning, 2008), as suggested by the presence of F-rich apatite and Na-rich minerals in the veins and their host rock (albite, paragonite, aegerine-jadeite).

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2.7

The behaviour of monazite: a petrological, trace element and SHRIMP U-Pb study of greenschist facies phyllites to anatectic gneisses, Chugach Metamorphic Complex, Alaska

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Monazite is a common accessory mineral in various metamorphic and magmatic rocks, and is widely used for U-Pb geochronology. However, linking monazite U-Pb ages with the PT evolution of the rock is not always straightforward. We would like to present the results of an investigation of the behaviour of monazite in a metasedimentary sequence ranging from greenschist facies phyllites into upper amphibolites facies anatectic gneisses. The sequence is exposed in the Eocene Chugach Metamorphic Complex of southern Alaska. We investigated the texture, chemical composition and U-Pb age of monazite in samples of differing bulk rock composition and metamorphic grade, with particular focus on the relationship between monazite and other REE-bearing minerals such as allanite and xenotime. In the greenschist facies phyllites, detrital and metamorphic allanite is present, whereas monazite is absent. In lower amphibolites facies schists, small, medium-Y monazite is wide-spread (Mnz1), indicating monazite growth at ~550°C and ≤3.4 kbar prior and/or simultaneous with growth of garnet and andalusite. In anatectic gneisses, new low-Y, high-Th monazite (Mnz2) crystallized from partial melts, and a third, high-Y, low-Th monazite generation (Mnz3) formed during initial cooling and garnet resorption. U-Pb SHRIMP dating of the second and third monazite generations revealed ages indistinguishable within error of the method and constrains these growth events to ~54-51 Ma. Monazite becomes unstable and is overgrown by allanite and/or allanite/epidote/ apatite coronas within retrograde muscovite- and/or chlorite-bearing shear zones. This study documents polyphase, complex monazite growth and dissolution during a single-phase, relatively short-lived metamorphic event. The successive generations of monazite are related to metamorphic stages using microtextural observations combined with petrology, trace element geochemistry and geochronology.

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Mo isotope composition of Mo-rich hydrothermal systems in the Aar Massif

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The investigation of Mo isotopes has become increasingly popular in geosciences in the last decade. As molybdenite (MoS_2) is the only industrially valuable Mo mineral source, a number of studies have focused on its Mo isotope composition (IC). In this study, we analyzed the Mo IC from two MoS_2 mineralizations (Alpjahorn and Grimsel) and from a Mo-rich hydrothermal breccia (Grimsel) to broaden our knowledge about the Mo isotope behaviour in magmatic and hydrothermal systems. The two MoS_2 occurrences are related to late-magmatic processes in connection to residual hydrothermal fluids from the intrusion of the Central Aar granite, whereas the breccia has a Pliocene age and the Mo was transported via oxidized surface waters into the breccia system. In both cases, a reduction of Mo let to its precipitation.

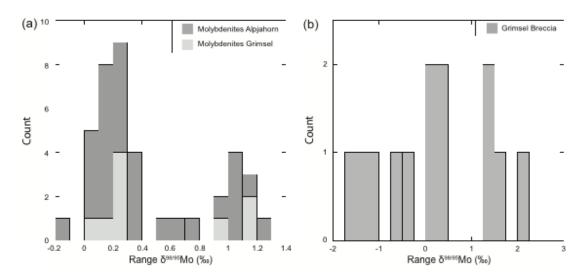


Figure 1. (a) Mo IC of MoS, from the Alpjahorn and the Grimsel Pass, showing two maxima. (b) Mo IC from the Mo-rich Grimsel breccia.

The breccia shows a wide and quite homogeneous Mo IC scatter of 3.0 ‰ (Figure 1). The P895Mo of the MoS₂ mineralizations varies over 1.35 ‰. Even in a single hand specimen it spans 0.45 ‰, indicating that fractionation processes during MoS₂ precipitation can vary on a cm scale. In contrast to the breccia, the MoS₂ of the Alpjahorn and the Grimsel Pass have an identical, bimodal Mo isotope pattern (Figure 1). This indicates that the same magmatic source and genetic evolution, in this case the intrusion of the central Aar granite, has formed both mineralizations. In addition, Rayleigh fractionation alone, as proposed in former studies, is unlikely to produce the observed bimodal Mo IC of molybdenites. Three explanations could account for this distinct Mo isotope signature of the MoS₂:

- 1. Alpine metamorphism might have caused additional Mo isotope fractionation. However, our petrographic observations do not hint at a redistribution of MoS₂.
- 2. If boiling of the hydrothermal fluid occurred, the transfer of dissolved Mo in a liquid hydrothermal phase and its uptake into a water vapour phase is also likely to produce Mo isotope fractionation. The precipitation of a first MoS_2 population from a vapour phase and of a subsequent one from a brine could account for the Mo IC pattern found in our samples.
- 3. The Central Aar granite has a Mo isotope value significantly lighter than that of most MoS_2 in the Aar Massif. The $\Delta^{98/95}Mo$ between granitic silicates and MoS_2 indicates that the former either preferentially incorporate light Mo isotopes during crystallization, or that hydrothermal fluids selectively precipitate heavy Mo isotopes. In either case, two discrete pulses of fluid exsolution from an increasingly fractionated magma could have produced the two isotopically different MoS_2 groups.

As reduction reactions are important considering Mo precipitation in both investigated systems (breccia and MoS_2), we suggest redox variations to be a main factor controlling the Mo IC in hydrothermal environments. To gain more information about the Mo fractionation processes in hydrothermal systems, the investigation of MoS_2 from the unmetamorph Questa porphyry deposit (USA) is in progress. Based on a detailed geochemical study, this deposit was formed by two different hydrothermal fluid exsolutions and should therefore help to deny or strengthen at least the $3^{\rm rd}$ hypothesis explained above.

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Percolation and impregnation of a plagioclase-rich melt into the mantlecrust transition zone of the Makran ophiolites, SE Iran

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The Makran ophiolites are situated to the north of the accretionary wedge formed in the subduction zone between Arabia and Eurasia. The ophiolite sequence comprises harzburgite with rare lherzolites as the structurally lowest unit intruded by troctolite and gabbros that were covered by lavas and sediments after exhumation. Dunites occur next to extensive mafic intrusions and in the upper levels of the main outcrops as remnants of melt percolation. They mostly show cumulate textures and are only little serpentinized. Meter thick impregnation zones and bands of all sizes where plagioclase is interstitial make the often transitional contact to the troctolite difficult to locate. Only chemistry allows distinguishing olivine crystallized from the plagioclase-rich melt, identifying the rock as troctolite from olivine equilibrated after melt percolation in impregnated dunite. Plagioclase impregnation zones, troctolite and gabbro dykes intruding the re-equilibrated dunite mark the transition from depleted harzburgitic mantle to a lower oceanic crust consisting of cumulate dunites and various mafic intrusions.

HREE enrichment in all samples is attributed to melt percolation. Typically, dunites show an almost V-shape REE pattern, since they are the product of re-equilibration after the melt percolated; accordingly, they are enriched in HREE and demonstrate a steeper LREE trend. Dunite crystallized in melt channels yield a strongly positive Eu anomaly, which reflects plagioclase crystallization. Clinopyroxene in harzburgite is depleted in HREE and shows a flat trend in LREE, while clinopyroxenes of olivine-orthopyroxenite dykes and dunite are more enriched in HREE, suggesting stronger melt influence. Trace element features of plagioclase in impregnations and troctolites are identical.

The Makran ultramafic rocks represent a piece of oceanic lithosphere that has been percolated by plagioclase-rich melt at less than 1km depth, equivalent to the pressure at which plagioclase crystallizes before clinopyroxene at an estimated temperature of ~1000°C. The troctolite is being dated with Sm/Nd to get the age of intrusion. Other temporal constraints were obtained by SHRIMP and La-ICP-MS measurements of U-Pb isotopes in zircons of a trondhjemitic (~ 145 Ma) and a peraluminous granite dyke (~ 111 Ma). Granite dykes possibly intruded after obduction, since the youngest sediment covers are Barremian (125-130 Ma).

Mass transfer processes and fluid composition of metamorphic quartz vein systems, Rhenish Massif (Germany)

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Formation of metamorphic veins in fold-and-thrust belts is generally related to crustal fluid flow and fluid-rock interaction processes (Yardley, 1983; Oliver & Bons, 2001). Fluid inclusions in metamorphic veins record the chemical composition of metamorphic fluids and their evolution with time. This project investigates the fluid chemistry and mechanisms of mass transfer in metamorphic vein systems in the Rhenish Massif (Germany) by combination of field studies, fluid inclusion studies, isotope geochemistry and geochemical modeling. The project is part of the multidisciplinary research initiative FRACS (www.fracs.de) that aims at understanding the dynamics of vein formation processes at a fundamental level, and involves strongly linked collaboration between structural geologists, material scientists, hydrologists and geochemists. Based on field documentation and structural mapping, the relative time sequence of deformation and vein forming events in the central part of the Rhenish Massif has been established. Hosted by wall rocks of monotonous slates, two main generations of metamorphic quartz veins were identified. These are (1) en-echelon vein sets with tension gash shape located in faults and shear zones, related to progressive compressional deformation, and (2) extension veins related to the late-orogenic stage with tabular shape, abundant open vugs and fissures (containing euhedral quartz crystals) and pronounced laterally extensive alteration zones. They crosscut almost perpendicular the slate foliation (S1) that has NE-SW striking direction and subvertical dip. The second vein type is particularly important, because it likely channelized major amounts of comparatively hot fluids (Wagner et al., 2010).

Following petrographic investigation, the fluid inclusion study has concentrated on the extension veins, because they host abundant fluid inclusions with suitable sizes for fluid inclusion microanalysis using LA-ICPMS, and they show a complex multi-stage filling and growth history. The different stages are characterized by distinct textures, with the early stage comprising elongate-blocky quartz (Bons & Jessell, 1997), which gradually evolves to the late stage characterized by euhedral crystallization of quartz. Combining microthermometric and LA-ICPMS microanalysis of different fluid inclusion assemblages, we were able to produce one of the first datasets of the solute inventory in low-grade metamorphic fluids.

The salinity of the fluids is rather low, being in the range between 3 and 5 wt% NaCl in all the fluid inclusions analysed. With LA-ICPMS it was possible to analyse the concentration of several major and minor cations in each fluid inclusion. As expected, most of the alkali and alkali earth elements like Li, Na, K, Rb, Cs, Sr, Ba and B show consistent concentrations in all fluid inclusion assemblages measured. The concentrations of Ca, Mg, S, Mn, Zn, Sb are more variable among assemblages, likely reflecting their comparatively low concentrations and associated rather large analytical errors. From the data it is possible to calculate the K/Na ratio, which is an important first-order indicator for the status of fluid-rock equilibrium during vein formation. This is because for aqueous fluids that are in chemical equilibrium with quartzo-felspathic rocks, the K/Na ratio strongly decreases with increasing temperature (Yardley 2005; Dolejs & Wagner 2008). Our data give average K/Na ratios of 0.025 ± 0.013 indicating equilibration of the fluids at temperatures of around 250 ± 30 °C, in good agreement with other independent temperature estimates for the formation of the late-stage euhedral quartz crystals (Wagner et al. 2010).

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Fluid chemistry and fluid-rock interaction of Alpine veins, Central Alps

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The classical Alpine fissure veins are large cavities lined by occasionally giant quartz crystals and many other euhedral mineral assemblages. They occur in regionally metamorphosed terranes in the upper crust and record important information about the composition and evolution of metamorphic fluids (Mullis, 1996) and fluid sources and mass transfer during crustal fluid-rock interaction (Oliver & Bons 2001). Detailed fluid inclusion studies of Alpine veins along a Geotraverse in the Central Alps have established that the fluid composition shows a distinct evolution with increasing metamorphic grade, where consecutive zones are dominated by (1) heavier hydrocarbons, (2) CH₄, (3) H₂O-NaCl, and (4) H₂O-CO₂-NaCl (Mullis et al. 1994). This study addresses the chemical evolution of fluids in Alpine fissure veins in the Central Swiss Alps by integrating field work, fluid inclusion studies (microthermometry and LA-ICPMS microanalysis of individual fluid inclusions), and geochemical modeling.

The field locations were selected along a cross section through the Central Alps that covers different lithologies and metamorphic conditions. This includes vein systems in the Aar massif (Gauli glacier, Gerstenegg vein in the Grimsel power station), the Nufenen and Griess pass, the Bedretto valley, and the Maggia valley. Fluid inclusion studies have been completed for the two localities in the Aar massif, and it was possible to analyze a considerable number of elements with LA-ICPMS. These include Na, K, Rb, Cs, Li, Ca, Mg, Sr, Ba, Mn, B, As, Sb, S, Pb and Zn. The fluid inclusions from the Gauli and Gerstenegg vein systems are low-salinity aqueous two-phase. While the Gauli samples contain fluid inclusions with 4.5-5.0 wt% equivalent NaCl, those from the Gerstenegg have a considerably higher salinity of around 10 wt% eqv. NaCl.

This difference in salinity is correlated with consistently higher concentrations of those elements that are largely complexed by chlorine such as the alkali and earth alkaline metals, and divalent transition metals (Yardley 2005). Consequently, the fluid inclusions from the Gerstenegg yielded consistent data for Pb, Zn and Ag on the order of few ppm, whereas the concentrations of these metals were mostly below the detection limit in the Gauli samples. We will expand the fluid inclusion studies to Alpine fissure veins in the southern part of the cross section that record a higher metamorphic grade.

Of particular interest will be to compare the solute composition of aqueous-carbonic fluids with those of the more simple aqueous H_2 O-NaCl type fluids. Comparing the measured fluid compositions with results from multicomponent-multiphase fluid-mineral equilibria modeling will then make it possible to evaluate the status of fluid-rock equilibrium along the metamorphic gradient.

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Pyroclast textures in the explosive 2007-2008 eruption of Oldoinyo Lengai, Tanzania: Implications for magma ascent and fragmentation

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After more than 25 years of effusive natrocarbonatitic activity the Oldoinyo Lengai (OL) volcano in northern Tanzania started erupting explosively in September 2007. The eruption continued for 8 months and was surprisingly vigorous (occasionally the plume reached up to 15 km in altitude). It has previously been proposed that thermal decomposition of older natrocarbonatites (and release of CO_2) inside the main crater of the volcano was responsible for the vigour associated with the explosive 1966-67 eruption.

From the recent eruption we sampled the initial ash-fall (3 days after the onset) in Al-canisters during a 24 hour period, which was later complemented by tephra samples collected from 140 profiles around the volcano during a field campaign in May 2011. Petrologically, bulk-rock analyses show a trend from being a mechanical mixture of natrocarbonatitic and nephelinitic material in the beginning of the eruption, to being dominated by nephelinitic composition at the end of the eruption.

SEM-studies of the first ash-deposits (i.e., September 7th) show a dominance of non-vesicular natrocarbonatitic droplets (containing nyerereite and gregoryite phenocrysts) mixed with a small amount of sub-spherical nephelinitic pyroclasts with low vesicularity (<25 vol.%). Deposits from the later phases of the eruption (as deduced from the tephra-stratigraphy) are dominated by well-sorted, near-spherical, lapilli. In these deposits, the natrocarbonatitic component is absent and individual tephra layers can be distinguished based on variations in grain-size. SEM studies of pyroclasts reveal that approximately 60% of the lapilli are cored by a crystal (predominantly nepheline, garnet, pyroxene, wollastonite) which is covered by a thin melt film. The nephelinitic melt film varies in vesicularity between 20 and 50 vol.% with a clear predominance of near-spherical vesicle shapes. An abundance of small particles and crystals are adhered/welded to the fluidal outer surface of the nephelinitic melt droplets. In addition to this, most of the studied deposits display an absence of particles produced by breaking/rupturing of vesicle walls.

Thus, the observed pyroclast textures in the OL-deposits strongly suggest that the nephelinitic magma was erupted in a similar fashion as an aerosol (i.e., melt droplets carried by a gas stream). Decomposition of carbonates which is required to generate such high gas-fluxes cannot occur inside the crater as this material is highly porous and only constitute the uppermost 80 m of the conduit (leaving little time for gas expansion to occur inside the conduit). Based on the observed pyroclast textures we find that the nephelinitic magma must have interacted with a deeper carbonatitic reservoir, in order to allow the CO₂ to expand during ascent (i.e., decompression). This interpretation is also supported by the petrological data.

2.13

The Kapan zone of the Somkheto-Karabakh island arc in the Lesser Caucasus: magmatism and ore deposits associated with Neotethys subduction

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The present-day Lesser Caucasus forms part of the Tethyan belt, which is the result of complex processes of ocean openings, subductions, obductions and micro-plate accretions. Long lasting northwards subduction of the Neotethys (e.g. Khain & Koronousky 1997) below the Eurasian margin caused the evolution of the Jurassic-Cretaceous island arc of the Lesser Caucasus. It can be divided into the northwest-southeast striking Somkheto-Karabakh island arc, extending over 600 km from southern Georgia over northern Armenia into Nagorno Karabakh, and the subparallel Kapan zone further to the southwest which extends over 100 km from southeastern Armenia into northern Iran (Figure 1).

A pile of up to 7000 m of volcanic and volcaniclastic rocks characterizes the Jurassic-Cretaceous island arc of the Lesser Caucasus. In the Kapan zone, three magmatic complexes are distinguished from each other, which are by name the Middle Jurassic, Upper Jurassic-Lower Cretaceous and the Paleogene magmatic complexes (Achikgiozyan et al. 1987). Intrusive rocks in the Kapan zone are rare but small bodies of gabbros and diorites occur. Most of the mineralization in the district is associated with the Middle Jurassic magmatic complex, minor uneconomic mineralization occurs in the unconformably overlying younger rocks. Other ore deposits along the Somkheto-Karabakh island arc such as the Drmbon deposit of Nagorno Karabakh or the Alaverdi deposits of northern Armenia are also related to similar volcanic and subvolcanic rocks of Middle Jurassic age.

Two different ore deposits are found in the Middle Jurassic volcanogenic complex of the Kapan mining district, distinct in mineral assemblage and host rock alteration: the Cu-Au-Ag-Zn±Pb Shahumyan deposit and the Cu±Au±Zn Centralni deposit are both located within a 4 km distance from each other. The currently operating Shahumyan deposit is hosted in subvolcanic quartz-dacite. Pyrite, chalcopyrite, sphalerite, fahlore and galena are the main ore minerals hosted in more than 100 east-west striking and steeply dipping extensional veins with phyllic alteration halos. Quartz and carbonates are the main gangue minerals. Gold and silver distribution in Shahumyan is controlled by different Au-Ag-tellurides. Northeast of the Shahumyan deposit, the abandoned Cu±Au±Zn Centralni deposit is divided into Centralni West and Centralni East. Centralni East and West are separated from each other by a major fault zone. Mineralization in Centralni West occurs in N100°±10° striking veins with variable 60°-80° dip to the south. Chalcopyrite and pyrite are the main sulfide minerals, together with minor amounts of fahlore and galena. Gangue minerals include quartz and carbonates. The orebearing volcanosedimentary sequence hosting the Centralni West mineralization is dark-green altered to chlorite, carbonate and epidote. Centralni East is characterized by stockwork-like mineralization within argillic altered andesite, with colusite, fahlore, chalcopyrite, minor luzonite and galena occurring as main ore minerals.

All magmatic rocks from the Middle Jurassic, Upper Jurassic-Lower Cretaceous and the Paleogene magmatic complex of the Kapan zone show subduction-related signature based on trace element geochemical data obtained by LA-ICP-MS analyses. However, igneous rocks of Middle Jurassic age can be distinguished from their overlying rocks by accentuated flat REE patterns and strong negative Nb- and Ta anomalies. A more depleted magma source and the pronounced participation of subduction-derived fluids during melt generation distinguish Middle Jurassic igneous rocks from the younger ones in the Kapan zone. In the subduction-related island arc of the Lesser Caucasus these processes might have been the key factors for the generation of fertile melts to which Middle Jurassic ore deposits are associated with.

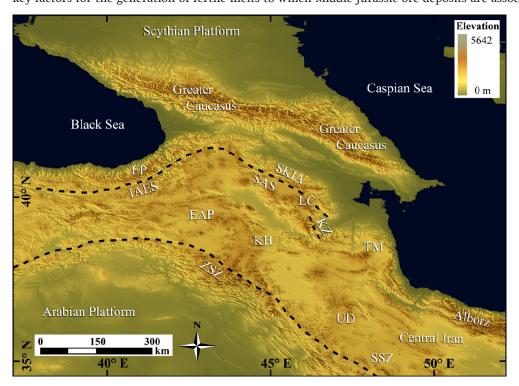


Figure 1. Digital elevation model of the Lesser Caucasus and adjacent regions. EAP-East Anatolian Platform; EP-Eastern Pontides; IAES-Izmir-Ankara-Erzinkan suture; KH-Khoy ophiolitic complex; KZ-Kapan zone; LC-Lesser Caucasus; SAS-Sevan-Akera suture; SKIA-Somkheto Karabakh island arc; SSZ-Sanandaj-Sirjan zone; TM-Talesh mountains; UD-Urumieh Dokhtar magmatic arc; ZSZ-Zagros suture

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Biogeochemical processes in sediments of the manganese nodule belt in the equatorial NE Pacific Ocean

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During RV Sonne cruise SO-205 to the eastern part of the German manganese nodule exploration area, located in the Clarion-Clipperton Fracture Zone of the Pacific Ocean, we recovered sediments with a multiple corer and a box corer at 14 sites and with piston and gravity corers at 7 sites. These samples were geochemically analyzed to elucidate whether diagenetic processes contribute to manganese nodules growth.

High-resolution oxygen measurements revealed an oxygen penetration depth of 2-3m. This finding is in contrast to previous assumptions, which suggested oxic sediments over several tens of meters (Müller et al., 1988). Manganese nodule abundance was determined from the box core samples. The sediments recovered with a piston-/gravity corer at the same sites show neither dissolved Mn²+ in pore waters nor denitrification in sediments from sites with medium to high manganese nodule abundance. In contrary, sediments from nearby locations with no nodules or low manganese nodule abundance show an increase of pore water [Mn²+] with depth and denitrification. This result suggests that there is no diffusive flux of Mn²+ from underlying sediments to manganese nodules at the surface (no suboxic diagenesis). Furthermore we propose that these small scaled regional differences in the geochemical characteristics of sediments can be explained with variations in sedimentation rates and organic matter input, which in turn are probably controlled by differences in bottom water current strength due to lateral variations in seafloor roughness or the occurrence of seamounts (Turnewitsch et al., 2004).

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Fluid composition and mineral equillibria in low grade metamorphic rocks, Bündnerschiefer, Switzerland. Application of fluid inclusions and petrological modeling.

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The composition of fluid inclusions hosted in quartz veins from low-grade metamorphic rocks of the Bündnerschiefer (north of Thusis and Schiers valley), Swiss Alps, was analyzed by combination of microthermometry and LA-ICPMS microanalysis. Massive milky quartz and euhedral quartz crystals were sampled form two sets of veins, which are foliation parallel veins and open fissure veins that crosscut the main foliation. The host rocks are organic-rich metapelites, that additionally contain relatively high amounts of carbonate in the case of Schiers. Several metamorphic temperature indicators were used to determine the temperature and pressure during metamorphism of the host rocks: Kübler index for illite (Kübler & Jaboyedoff 2000), Raman spectroscopy on carbonaceous material (Beyssac et al. 2002), mineral assemblages, chlorite geothermometry (Cathelineau 1988), and Na-Mg fluid solute geothermometry (Giggenbach 1988). All geothermometers point to equilibrium temperatures around 320 ± 20 °C for the Thusis rocks, placing them into the lower epizone (lower greenschist facies). The samples from Schiers show anchizone (subgreenschist facies) characteristics and have been metamorphosed at temperatures around 250 °C ± 20 °C. Most of the important rock forming elements have been successfully determined in individual inclusions. The fluid inclusions show very consistent element concentrations within petrographically defined fluid inclusion assemblages. They contain measurable concentrations of Na, K, Rb, Cs, Li, Ca, Mg, Mn, Sr, Ba, B, As, B, Zn, Pb, Cu and S. Typical elements concentrations are: Al (Thusis 30-40 ppm), Mg (Thusis 5-7 ppm, Schiers 3 ppm), Ca (Thusis 300-400 ppm, Schiers 200 ppm), Mn (both places 3-5 ppm), S (Thusis 300-350 ppm, Schiers 150 ppm), and Cu (Thusis 5-20 ppm) as well as the fluid inclusions have salinities of -2.3 ± 0.1 °C at Thusis and -1 ± 0.1 °C at Schiers. Homogenization temperatures are 122 to 140 °C at Thusis and 82 to 86 °C at Schiers. The total element concentrations are lower compared with bulk crush leach fluid composition data from similar metamorphic vein settings, and considerably lower than in mesothermal gold ore deposit fluids (Yardley et al. 1993; Yardley 2005). This likely reflects the lower bulk salinity of fluids in the Bündnerschiefer veins, which exerts a major control on those elements that are complexed by chloride (Yardley 2005). Combining fluid inclusion isocores with independent geothermometers results in pressure estimates between 2.8 and 3.8 kbars for Thusis, and around 3.4 kbars for Schiers. The geothermal gradient decreases from the southern location (27-22 °C/km: Thusis) to the northern location (19 °C/km: Schiers). The results of pseudosection modeling using Perplex (Connolly & Petrini 2002) show very close agreement between calculated and measured mineral assemblages and mineral modes, and further constrain the pressure-temperature conditions that were derived from conventional geothermobarometry. The fluid inclusion data, in conjunction with metamorphic indicators and petrological modeling suggest that fluid-rock equilibrium was reached during metamorphism. The comprehensive fluid composition dataset obtained in this study can be further used for fluid-rock equilibrium calculations and for improving mineral and fluid speciation thermodynamic models.

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Major Cu, Au and Mo deposits of the Lesser Caucasus: Products of diverse geodynamic settings

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The Lesser Caucasus sits astride on Georgia, Armenia and Azerbaijan, and is a favourable environment for investigating the formation of diverse ore deposits in successive geodynamic settings. It combines an evolution ranging from Jurassic-Cretaceous compressive tectono-magmatic events in subduction, Andean-style environments to Neogene, post-collisional, extensional tectono-magmatic events. The geodynamic evolution was accompanied by episodic ore formation in response to particular tectonic and/or magmatic events, which vary in style as a function of the different geodynamic settings. Recent studies in Anatolia, the Caucasus and Iran have improved our understanding about the Mesozoic to Tertiary geodynamic evolution of the Tethys orogenic belt. It formed during convergence and collision of the Eurasian, Arabian and African plates, in a complex setting including abundant microplates. Such contributions allow us to investigate the formation of ore deposits in a well-defined, regional geological framework. Ore deposit formation in the Lesser Caucasus occurred episodically. If one excludes basement rocks, four main metallogenic events can be distinguished: Middle-Late Jurassic, Late Jurassic-Early Cretaceous, Late Cretaceous, and Tertiary. Recent geochronological, lithogeochemical, and stable and radiogenic isotope data yield new constraints about the timing and genetic interpretations of various ore deposits during the geological evolution of the Lesser Caucasus.

The earliest metallogenic event consists of gold- and telluride-bearing, copper-rich pyrite veins and massive ore bodies hosted by Middle Jurassic volcanic and volcano-sedimentary rocks of the Somkheto-Karabakh island arc, with a mostly calc-alkaline composition. These deposits (Kapan, Alaverdi, Drmbon) remain the most enigmatic ones within the Lesser Caucasus, and it is debated whether they are volcanogenic massive sulphide (VMS) deposits, hydrothermal veins emplaced in a large volcanic edifice, or porphyry-style deposits. Middle to Upper Jurassic, and younger Cretaceous and Tertiary ages have been proposed. Sulphur isotopic compositions of barites mostly deviate from the ones of coeval Jurassic seawater, therefore questioning a typical VMS-only scenario.

The second metallogenic event consists of Cu-porphyry, skarns and epithermal gold deposits also located in the Jurassic-Cretaceous Somkheto-Karabakh magmatic arc, formed during subduction of the Neotethys below the Eurasian margin. They are mostly interpreted as Upper Jurassic to Lower Cretaceous in age, which is confirmed by a recent Re-Os molybdenite age of 145.85 ± 0.59 Ma and Rb-Sr isochrone ages of 156 ± 3 and 164 ± 6 Ma for the Teghout area, Armenia. Several porphyry copper deposits in include zones of massive sulphide lenses, locally enargite, alterations consisting of silicification, sericite, kaolinite, and alunite, and gold-enrichments typical for deep porphyry to shallow epithermal transitional environments.

Upper Cretaceous volcano-sedimentary units, with abundant felsic volcanic and sub-volvanic rocks in an extensional setting including caldera formation, host polymetallic base and precious metal deposits, and mark the onset of arc rifting of the Somkheto-Karabakh belt and its Variscan basement, as documented at the Madneuli polymetallic deposit, Georgia and adjacent precious metal epithermal deposits. K-Ar and microfossil dating of the host rocks indicate, respectively, Coniacian - Middle Campanian and Middle - Upper Campanian ages. Detailed lithofacies studies document a mostly shallow marine depositional environment of the Madneuli host rocks. Lithogeochemistry of the magmatic rocks reveals a composition transitional between calc-alkaline and tholeitic. The sulphur isotopic composition of ore sulphides and barite are consistent with magmatic and coeval Late Cretaceous seawater, respectively. Sr isotope data reveal a more radiogenic composition of the magmatic rocks at Madneuli (87Sr/86Sr = 0.7046-0.7075) in contrast with lower 87Sr/86Sr ratios (<0.7046) of the older Upper Jurassic - Lower Cretaceous magmatic rocks (see above) and the younger Tertiary magmatism (below). We conclude that these deposits are bimodal-felsic VMS-type deposits (Kuroko-Baimak) formed in a magmatic arc underlain by a continental basement, with transitional features to epithermal deposits, as recognised elsewhere in the Eastern Pontides.

The Tertiary evolution of the Lesser Caucasus is dominated by collisional and postcollisional tectonics and magmatism. The most important mineral district is the Tertiary Zangezur-Ordubad block (Meghri composite pluton) in the southern

Caucasus, close to the Iranian border, which consists of Eocene to Miocene calc-alkaline to alkaline mafic to felsic magmatic suites, and which hosts major Mo-Cu-porphyries (including the world-class Kadjaran deposit) and subsidiary precious and base metal prospects. High-precision U-Pb zircon TIMS ages confirm the pulsating nature of magmatism revealed by previous Rb-Sr isochrone ages, with an early Eocene event (40-45 Ma) followed by events during the Oligocene (30-32 Ma) and the Miocene (20-23 Ma). On-going, high-precision Re-Os molybdenite dating from different Mo-Cu porphyry deposits indicate discrete ore forming events at 40-44 Ma (Agarak, Aygedzor, Dastakert deposits), 31 Ma (Kaler) and 27 Ma (Kadjaran), essentially overlapping with magmatic events. Studies are ongoing to understand the long duration of about 20 m.y. of repeated ore-forming processes in the postcollisional context of the Meghri pluton, as a result of slab break off and asthenospheric upwelling.

Postcollisional Tertiary magmatism is also at the origin of abundant, but poorly characterized epithermal gold deposits and prospects of the Lesser Caucasus, with uncertain Eocene to Miocene ages. Both low-sulphidation (e.g. Zod-Sotk, Miocene in age, mainly hosted by Jurassic ophiolites) and high-sulphidation deposits (e.g. Amulsar, best world gold discovery in 2006) are recognized.

2.17

PVTX evolution and reequilibration of prograde and retrograde fluid inclusions in diagenetic and metamorphic rocks, Central Alps, Switzerland.

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Careful fabric, host mineral and fluid inclusion analyses of several hundred localities of the external parts of the Central Alps enable a critical discussion about their application to fluid evolution and fluid thermobarometry. Detailed investigations on fluid inclusions formed during prograde, PT-maximum and retrograde conditions in vein, Alpine fissure and slickenside systems from diagenetic to metamorphic terrains have been carried out.

Once trapped, fluid inclusions may re-equilibrate by changing their volume and content. This occurs by stretching, leakage and decrepitation of fluid inclusions when fluid pressure largely exceeds the confining pressure during further burial (e.g. McLimans 1987) and during heating (Mullis 1987; Tarantola et al. 2007). Fluid inclusions are reset by static or dynamic recrystallization of the host minerals (e.g. Wilkins and Barkas 1978). Furthermore, fluid inclusions are also modified under deviatoric stress and post entrapment ductile deformation (Tarantola & Diamond 2010). During retrograde evolution, stretching and decrepitation of high dense fluid inclusions might occur by isothermal pressure drop (Mullis 1987).

Our observations show that:

- 1. Fluids trapped at an early stage along the prograde path have mostly left the host mineral, due to fluid overpressure, decrepitation and recrystallization. Remaining fluid inclusions do not reflect composition and density of the fluid trapped during mineral growth.
- 2. Only very small fluid inclusions formed during prograde temperatures might be preserved and could reflect the prograde fluid composition, as recrystallization is not complete.
- 3. Hydrocarbon-saturated water-rich and water-saturated hydrocarbon-rich fluid inclusions formed at *PT*-maximum and during retrograde conditions are of reliable quality for geothermometry and geobarometry.
- 4. Fluid inclusions exposed to conditions of larger confining pressures than internal fluid inclusion pressure show tridimensional implosion features, and do not reflect the original trapping density.
- 5. Fluid inclusions exposed to post-entrapment ductile deformation by deviatoric stress form a bidimensional halo of neonate inclusions, revealing possible densities of the involved shearing event.
- 6. High dense fluid inclusions that were stretched or decrepitated by local and temporary pressure drop during retrograde conditions (due to seismic pumping or seismic valving) do not reflect the true composition and density of the original fluid.
- 7. High dense fluid inclusions that were stretched or decrepitated during "isothermal" uplift do not reflect composition and density of the original fluid.

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2.18

Density of alkaline magmas at crustal and upper mantle conditions by X-ray absorption

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Silicate melts are essential components of igneous processes and are directly involved in differentiation processes and heat transfer within the Earth. Studies of the physical properties of magmas (e.g., density, viscosity, conductivity, etc) are however challenging and experimental data at geologically relevant pressure and temperature conditions remain scarce. For example, there is virtually no data on the density at high pressure of alkaline magmas (e.g., phonolites) typically found in continental rift zone settings.

We present *in situ* density measurements of alkaline magmas at crustal and upper mantle conditions using synchrotron X-ray absorption. Measurements were conducted on ID27 beamline at ESRF using a panoramic Paris-Edinburgh Press (PE Press). The starting material is a synthetic haplo-phonolite glass similar in composition to the Plateau flood phonolites from the Kenya rift [1]. The glass was synthesized at 1673 K and 2.0 GPa in a piston-cylinder apparatus at ETH Zurich and characterized using EPMA, FTIR and density measurements. The sample contains less than 200 ppm water and is free of CO_2 . Single-crystal diamond cylinders ($\emptyset_{in} = 0.5$ mm, height = 1 mm) were used as sample containers and placed in an assembly formed by hBN spacers, a graphite heater and a boron epoxy gasket [2]. The density was determined as a function of pressure (1.0 to 3.1 GPa) and temperature (1630-1860 K) from the X-ray absorption contrast at 20 keV between the sample and the diamond capsule. The molten state of the sample during the data collection was confirmed by X-ray diffraction measurements. Pressure and temperature were determined simultaneously from the equation of state of hBN and platinum using the the double isochor method [3]. The results are combined with available density data at room conditions to derive the first experimental equation of state (EOS) of phonolitic liquids at crustal and upper mantle conditions. We will compare our results with recent reports of the density of dry and hydrous rhyolite melts (Malfait et al., this meeting [4]) and discuss compositional effects on the density of melts and the implications for magmatic processes in the lower crust and magma chambers.

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Application of high-precision U-Pb geochronology to igneous petrology and stratigraphy: Potential and limitations

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High-precision U-Pb geochronology of accessory minerals is an integral part of various Earth Science disciplines. Recent advances in U-Pb geochronology by isotope dilution – thermal ionization mass spectrometry (ID-TIMS) allow dating of high uranium accessory minerals (most commonly zircon) at permil precision and external reproducibility. Such high temporal resolution may result in complex zircon age populations, reflecting prolonged growth and magma residence, previously only resolvable by in-situ U-Th dating in Pleistocene magmatic systems. This allows to track the evolution of Cenozoic magmatic systems at unprecedented resolution and to add absolute time constraints to thermal and petrogenetic models (Crowley et al., 2007; Schaltegger et al., 2009). However, these complexities have also been considered to systematically bias zircon U-Pb derived eruption ages, to compromise chronostratigraphic applications of high-precision zircon U-Pb geochronology and to contribute to the systematic offset between the K-Ar and U-Pb systems (Simon et al., 2008; Renne et al., 2010). With this contribution, we aim to highlight [1] the potential of high-precision U-Pb geochronology in igneous petrology and [2] limitations for stratigraphic applications arising from pre-eruption residence time.

We obtained a large number of high-precision zircon U-Pb dates for some of the best-studied Cenozoic magmatic systems, i.e. the ~28 Ma Fish Canyon Tuff (Colorado, USA) and the ~56 Ma Skaergaard intrusive complex (East Greenland). In both cases, zircon U-Pb dates record 300,000 to 400,000 years of crystallization. Combined with zircon trace element and oxygen isotope geochemistry, respectively, high-precision zircon U-Pb dates provide snapshots of magma evolution. Chemical or isotopic differences within zircon populations as a function of age allow us to construct time-integrated petrogenetic models within the framework of independent petrologic constraints and thermal models.

In stratigraphic applications, where the desired age information is that of ash bed deposition, the pre-eruptive magmatic history recorded by zircons is a fundamental limiting factor. We present high-precision zircon U-Pb dates from ash beds intercalated with astronomically tuned Miocene sediments, aiming to quantify the effect of prolonged crystallization on zircon U-Pb derived ash bed deposition ages. All ash beds yield complex zircon age populations recording prolonged crystallization at the 10-100 ka scale. While the majority of zircons predate eruption, in most cases the youngest closed system zircons yield ²⁰⁶Pb/²³⁸U dates indistinguishable from the respective astronomical age and thus accurately date ash bed deposition. However, the conventional approach of averaging statistically equivalent zircon U-Pb dates to increase precision tends to overestimate the deposition age, if complexities are masked by uncertainties of individual analyses. We conclude that the precision of ash bed deposition ages is limited to the precision of individual single grain analyses.

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Recent increase in Uranium Concentration in Lake Geneva Sediments: increased Inputs or enhanced chemical Precipitation?

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Uranium concentration in Lake Geneva water is relatively high (1.6 μ g U L¹) compared to other freshwater bodies, due to a partly granitic, uranium-rich watershed. Moreover, intense works to collect and transport glacial melting waters to hydroelectric reservoir have enhanced the mobilization of U-enriched zones (Dominik et al. 1992). In order to reconstruct the uranium historical evolution in Lake Geneva, four sediment cores have been ¹³⁷Cs dated and analyzed using ICP-MS for their trace element composition. One core was recovered close to the Rhone River mouth (T52, 145 m depth; Fig. 1), whereas the other cores were collected in the deepest part of the lake (> 300 m depth, Fig. 1). The core close to the Rhone mouth didn't show any noticeable increase in U concentration during the last 50 years. On the other hand, the three sediment cores retrieved from the deep lake showed a clear increase in U concentration by a factor 2 to 3, with concentrations rising from 1 - 2 mg/kg to 4 - 5 mg/kg (Fig. 1). ¹³⁷Cs dating revealed that this increase occurred in the late 70's and was synchronous in the deep lake.

This period corresponded to the onset of two processes that could explain this variation: i) the increase in U inputs due to the large development of the water derivation in the watershed (tunnel under the Mont Blanc massif to Emosson dam), and ii) the eutrophication of the lake that induced increased flux of organic matter and hypoxia to anoxia in the deep lake, which can favor the precipitation of dissolved U. To decipher the origin of this U concentration increase, a mass balance model has been developed, to simulate the effect of the observed increased dissolved U inputs from the watershed. Results of the simulation showed that the additional dissolved load corresponded to an increase of about 2% of U in the lake water after 30 years, so that the observed enrichment in U might not be related to an increase in the source. Moreover, no U increase has been observed close to the Rhone river mouth which is the major tributary of the lake, then an increase of the particulate flux can be excluded. Therefore the other explanation pointed to an internal physicochemical origin for the enhanced U concentrations measured in Lake Geneva sediments. Eutrophication of the lake reached a maximum in the 70's, with extended periods of hypoxia in the deepest water layers. These conditions also occurred between 1986 and 1999, due to the absence of complete lake overturn. It is hypothesized that these hypoxic conditions favored the chemical precipitation and settling of dissolved form of uranium. Despite a marked increase in the U concentrations, the additional contribution to the sediments due to the eutrophication (200 kg/y) was minor compared to the dissolved U flux from the watershed (12500 kg/y).

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P 2.2

Monazite and Allanite's textural evolution from lower to higher grade pelites of Miyar Valley, NW India

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The Himalayan metamorphic belt is a classic example of continent-continent collision (before 50-55 Ma), where ~1800-2500 km crustal shortening has occurred between the two plates of Indian and Eurasian. Number of thrust bounded slices has been developed within which the Higher Himalayan Crystalline (HHC), a 5-10 km thick sequence of amphibolite facies to migmatitic paragneiss preserves the metamorphic core of this orogen in Zanskar Himalayan terrain. The studied Miyar Valley section (Zanskar, NW India) consists of a single stratigraphic sequence of metapelites and -psammites which preserves a progressive increase in metamorphic conditions from the chlorite zone to the sillimanite zone and then in further migmatitic domain (Steck et al., 1999; Robyr et. al., 2002; Robyr et al., 2006) (Fig. 1). The main aim of this work is to document any systematic variations in the chemistry and the texture of the identified accessory minerals and to estab-

lish the possible reaction path for the monazite formation. The extensive thin section study of this area reveals that the occurrence of the first metamorphic monazite coincides with the disappearance of allanite grains in metapelites. It should be emphasized that this transition in the stable LREE accessory phases occurs at the level of the staurolite-kyanite-in isograd, regardless whether the samples were collected in psammitic or pelitic layers. This observation strongly suggests that the LREE budget required for the monazite forming reaction is provided primarily by the breakdown of allanite. Textural observations indicate that the size and the complexity of the zoning pattern of the monazites significantly increase with the gradually increasing grade along the metamorphic field gradient. Below the sillimanite-in isograd, the size of the monazite grains generally does not exceed 50 µm, and the grains display no clear chemical zonation. Above the sillimanite-in isograd, the monazite grains preserve a complex zoning pattern, and the size of the grains is around 250-300 µm, where in further migmatite zone after muscovite out isograd, it may reach 400-500 µm having most complex zoning pattern. Allanite and monazite along with apatite also have been found as inclusions within garnet of the sillimanite zone rock, which strongly suggest that these allanites are from garnet zone captured within it. This textural arrangement is of major interest since it should permit the identification of an accurate P-T-t path for this specific garnet. The significance of this complex zoning and if there is any significant role of major silicates in formation of monazite are needed to assess further.

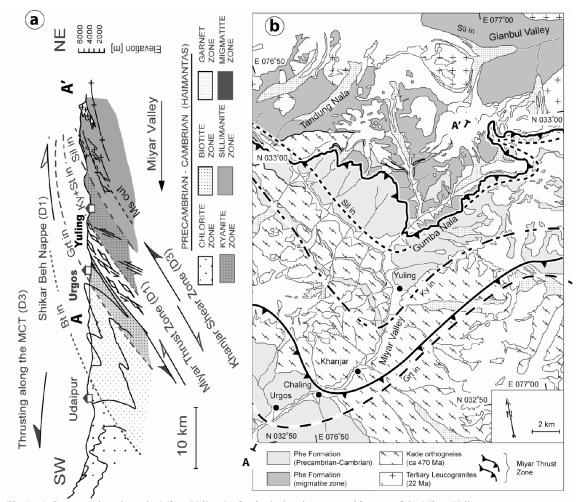


Fig.1: a) Cross-section along the Miyar Valley, b) Geological and metamorphic map of the Miyar Valley

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Explosion intensities and fragmentation modes of the Loolmurwak and Eledoi maar volcanoes, Lake Natron – Engaruka monogenetic field, northern Tanzania

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Two different theories currently exist on the explosion mechanism that is associated with diatreme volcanism. Some authors advocate a 'dry' eruption scenario in which gas exsolved from rising magma causes explosive activity, whereas others prefer a phreatomagmatic course of events in which diatreme formation is the result of interaction between magma and ground or surface water. However, only the later eruption mechanism is currently held viable for maar volcanoes, even though they are commonly, if not inevitably, associated with diatremes.

The Eledoi and Loolmurwak maars (Lake Natron - Engaruka monogenetic field, northern Tanzania) form two of the largest craters in an area of more more than 100 cones. Preliminary field evidence is in line with a recent study of Mattsson & Tripoli (2011) and suggests that craters in this area provide little evidence of wet deposition, such as accretionary lapilli and vesiculated tuffs. Rather, several observations point towards a dry mode of deposition, including a presumably wind-induced asymmetry of the crater rim (Eledoi) and the dominance of sub-spherical armoured lapilli, the core of which consists of olivine, pyroxene or amphibole phenocrysts (Loolmurwak, Fig. 1). Many of these lapilli show flattening parallel to the bedding plane, suggesting that they were molten droplets at the time of the eruption.

Magmas of both Loolmurwak and Eledoi are nephelinitic or olivine melilititic in composition. The abundance of phlogopite and amphibole megacrysts (up to 11 and 20 cm in diameter, respectively) indicates a high volatile content. Common in especially the Eledoi deposits is the occurrence of mantle xenoliths (predominantly dunites and wehrlites) that are frequently cut by several generations of metasomatic veins (containing amphibole, phlogopite, clinopyroxene and spinel). Mantle xenolith sizes suggest a minimum average magma ascent rate of 0.9 ms⁻¹ for the Eledoi eruption.

The rapid ascent rate of the involved magmas from upper-mantle depths and the exsolution of abundant volatiles, together with pyroclast shapes and textures that indicate 'dry' magmatic fragmentation and deposition, indicate that the emplacement mechanism of the Eledoi and Loolmurwak maar craters is very similar to that typical for many kimberlites. Consequently, a more detailed study of pyroclast textures, mineralogy and chemistry of the Eledoi and Loolmurwak deposits can provide valuable new insights into maar emplacement processes.

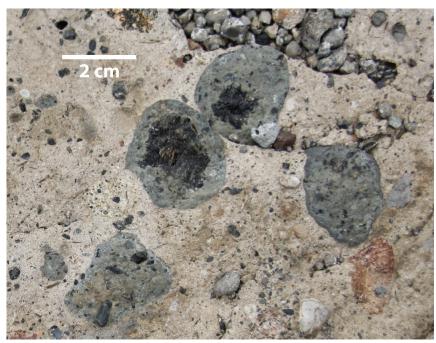


Figure 1. Subspherical armored lapilli within an ash matrix (Loolmurwak maar deposits). Lapilli cores predominantly consist of amphibole, pyroxene and olivine. Picture by J.F. Berghuijs.

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Stratigraphy and sedimentology of the Cretaceous host-rocks of the Madneuli gold-polymetallic deposit, Lesser Caucasus, southern Georgia: A new approach

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The Madneuli gold – copper – polymetallic deposit is located in the Bolnisi volcano tectonic depression between the Khrami and Loki pre-Alpine basement massifs. It is hosted by Cretaceous volcanic and volcano – sedimentary strata. In spite of intensive investigation and study of the deposit since its exploration in 1958, its origin is still debated. Recognition of sedimentary facies units within volcanic settings and especially those hosting ore bodies, based on process – oriented sedimentation has been neglected so far in our study area.

Our new sedimentological study of the Madneuli host rocks is focused on field and facies oriented analyses, and is based on the concept of flow transformations (gravity, body and surface types) that links the general volcaniclastic facies (single event) within a space – time framework from source to final deposition (proximal to distal, syn-, inter – or post eruptive, Fisher and Schminke, 1994). Based on this approach, we identified stratified tuff and lapilli tuff, subsidiary breccia – conglomerate and conglomerate – sandstone, slide – slump, accretionary lapilli-bearing tuff and tuffaceous units within the open pit and surrounding areas. Previous observations by Popkhadze et al. (2009) were confirmed and some were reinterpreted. The common transport mode operating within the area was deposition of volcanic and volcaniclastic – epiclastic material by debris, pyroclastic and ash flows, in some cases with flow transformation into density turbidity currents. Slide – slump units indicate downslope movement of sediments, either along the volcano flanks triggered by volcano – tectonic events or gravitational slumpling within debris apron environments. Graded layers of accretionary lapilli and ash represent airfall pyroclastic deposits, interlayered with non-fall layers with current structures suggesting entering moving water. Bouma sequences developed in these layers are not related to transportation by turbidites (Lowe, 1988). Tuffites associated with slump units are interpreted as alteration of lapilli and fine ash – flow tuffs and might reveal a hemipelagic environment during deposition. Red – brown polymict volcaniclastic - epyclastic conglomerates and sandstones are products of channelized mass flow deposition.

In volcanic environments, volcanic eruptions control facies stratigraphy and geometry. Thus, stratification and correlation of the rocks units within the Madneuli ore field is complicated and is reflected in rapid lateral and vertical changes, with abundant structural – volcanic unconformities, poor fauna preservation, and lack of modern precise radiochronological data. The combined stratigraphic subdivision of the Cretaceous suites of the area is based on two different schemes used by Gambashidze et al. (1987) and Vashakidze et al. (1998). It also includes recent data based on a nanofossil study of the host rocks (Gavtadze et al., 2006) and existing K-Ar geochronological data. Our study clearly shows incompatibilities between the boundaries of the suites and in some cases their debatable ages. Modern stratigraphic studies are based on the fundamental understanding of global sedimentary and tectonic processes. That is why we suggest to define stratigraphic units on the basis of basin – wide relationships by paying great attention to the regional framework.

We conclude that detailed and complex stratigraphic – sedimentological study within the Madneuli ore field together with litho – and biostratigraphic, seismic, subsurface and basin mapping methods is essential in correct subdivision of the rock units.

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Evolution of composition, temperature and pressure of fluid inclusions through the NEAT Lötschberg base tunnel

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The present research project is part of a multi-faceted research programme along the new alpine railway transverses NEAT. This project focuses on the investigation on fluid inclusions in the Lötschberg NEAT tunnels and boreholes.

Fluid inclusions are witnesses of the fluids from which the Alpine minerals precipitated in Alpine fissures several million years ago. Alpine fissures are generally small, closed ore opened hydrothermal systems that document the evolution of deformation, fluid composition, temperature and pressure during uplift and cooling (erosion) of the surrounding rocks.

The following aims are envisaged:

- 1. to understand the evolution of fluid composition, temperature and pressure during uplift and cooling along the Lötschberg transsect;
- 2. to recognize the origin of the mineralizing fluids.

Microthermometric investigations on fluid inclusions in fissure quartz from boreholes, shafts and tunnels along the NEAT Lötschberg transsect yield the following preliminary results:

- 1. Fluid composition evolves from higher hydrocarbon-bearing fluids (HHC-zone) close to Frutigen to methane-bearing fluids (methane-zone) at around 2 km South of Frutigen. Water-rich fluids with less than 2 mole % of $\mathrm{CH_4}$ and $\mathrm{CO_2}$ are characteristic for the sedimentary cover of the Northern Gastern Granit and all crystalline rocks of the Gastern and Aar massifs (water zone). The transition from the methane- to the water-zone occurs below the valley of Gasteretal. Up to 5 mole-percent of $\mathrm{CO_2}$ within fluid inclusions are diagnostic for the Triassic metasedimentary cover of the Soutwestern Aar massif.
- 2. Temperature and pressure develop from the HHC-zone at ≤ 150 °C and ~ 1.5 kbar to the HHC-methane transition at 200±5 °C and 2 kbar (Mullis 1979). The formation of methane is interpreted to be the maturation product of higher hydrocarbons, due to "burial" or "overthrusting". Methane break down occurs at 270 °C, due to redox-reactions between iron three bearing phyllosilicats and methane (Mullis et al. 1987; Tarantola et al. 2007). The dominance of aqueous saline fluids in the Gastern and Aar massifs is controlled by the lack of organic matter, dehydration reactions, as well as water-bearing metasediments situated probably below the massifs (Mullis et al. 1994). The increase of CO₂ in the Triassic metasedimentary cover is probably due to decarbonation reactions or oxidation of organic matter at temperatures and pressures of around 400 °C und 3.5 kbar.

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Geology of Piz Duan: an oceanic sequence in the Avers schists, Grisons

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A sediment-rich ophiolite unit can be mapped in the southern part of the Avers schists N of Val Bregaglia (southern Grisons). This so-called Duan-Cam unit (DCU) has a lenticular shape and is outlined by small lenses of serpentinite against the adjacent rock units. Its internal structure shows strong imbrication and folding, but the stratigraphic sequence is coherent and consists of three main rock types. The surrounding units (Avers schists above, Suretta nappe below) have a similar grade of deformation and metamorphism.

The main rock types comprise greenschists, banded quartz schists and calcite marbles. They represent the sequence of metamorphic basalt, radiolarite and limestone (pers. comm. P. Nievergelt). Both, the stratigraphy as well as preserved submarine volcanic structures (pillow lava) allow the DCU unit to be interpreted as a relic of an oceanic sequence in greenschist facies. These interpretation is confirmed by geochemical analysis which indicate a mid-ocean ridge basalt as protolith of the basic rocks. However, some of the metabasic rocks no longer show the original basaltic chemistry. These glaucophane-bearing metabasalts (prasinites, spilites) underwent strong oceanic hydrothermal alteration (Fe and Naenrichment, Oberhänsli 1978).

The Duan-Cam unit is situated in the footwall of the Turba mylonite zone (TMZ) (Nievergelt et al., 1996), less than 1 km below this shear zone. The deformation of the Avers schists includes shearing to the SE and finally the development of the TMZ with top to the E movement. Five deformation phases (D1–D5) can be distinguished in the DCU, two of which (D2 and D3) are related to the TMZ. D1 and D2 are strong deformation events, which caused isoclinal folding, penetrative foliations and imbrication. The structures of D1, which were formed during mesoalpine nappe stacking (Schreurs, 1995),

have been largely overprinted by D2 structures. Phases D3 to D5 show increasingly weaker deformation from narrow folding to kinking. Apart from D3 all deformation phases within the DCU can be correlated with deformation events postulated by researchers for the surrounding units, e.g. in the Austroalpine-Pennine boundary (Liniger & Nievergelt, 1996), the Suretta and Tambo nappe (Huber, 1996), Schams nappes (Schreurs, 1995). In contrast, the prominent D3 phase, which shows open to narrow folding with developing axial plain foliation, seems to be a local structural phenomenon, which cannot be observed in the surrounding units. Whereas the prominent D2 overprint is a consequence of the main extensional episode of the TMZ, it is assumed that D3 was generated by a second, slightly weaker Turba extension event, which only affected the directly underlying DCU.

The most conspicuous formation of new minerals took place during early deformation of the DCU. Glaucophane was formed late post-D1 to syn-D2 and altered syn-D2 to barroisite under retrograde metamorphic conditions. Stability fields of glaucophane and barroisite (Ernst, 1979) indicate P-T conditions of 6.5 kbar and 400 °C for D2. Rutile occurs as inclusion in glaucophane and was therefore formed syn-D1. Similar to the Zermatt-Saas region in the Western Alps the occurrence of glaucophane and rutile could be a relic of a high-pressure metamorphic event (Dal Piaz & Ernst, 1979). Furthermore pseudomorphs after an unknown syn-D1 formed mineral can be observed. These facts indicate to a metamorphic evolution that started earlier than reported so far in this area. However, because of the absence of additional high-pressure indicative minerals like e.g. lawsonite, unequivocal evidence for high pressure metamorphism in the DCU cannot yet be verified.

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Ordovician mafic magmatism in the Métailler Formation of the Mont-Fort nappe (Middle Penninic domain, western Alps) – geodynamic implications

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The Métailler Formation belongs to the basement of the Mont-Fort nappe, in the Middle Penninic domain of the western Alps. It consists of a heterogeneous volcanic detrital sequence dominated by mafic components including pillow-lavas and banded gabbros bodies. The age and significance of these lithologies have been debated since more than 50 years (e.g. Schaer, 1959; Chessex, 1995). These rocks have been strongly reworked by Alpine metamorphism and deformation in the greenschist facies. Metagabbro bodies are outcropping in the small Louvie valley, SE of Verbier (Wallis). They are composed of multiple coarse-grained bands (20cm to 5m thick) (Fig. 1a) of close but distinct chemical composition. Cm-long dark spots made of an actinolite \pm chlorite \pm epidote assemblage mimic former magmatic pyroxenes. These textural features as well as the shape and position of the gabbro bodies within the sedimentary host-rock suggest a sill-on-sill emplacement style in the volcanic-detrital sequence.

Magmas have a composition of continental tholeites of E-MORB type, including differentiated facies as Ti-rich gabbros. Small volumes of albite-rich evolved liquids form discordant dikelets or segregates within the gabbros and contain zircons. The latter show unusual sponge-like textures (Fig. 1b) interpreted as the result of a metamorphic dissolution-recrystallization process triggered by Na-rich fluid circulation during Alpine metamorphism, in a similar way as described by Rubatto et al. (2008). LA-ICPMS U-Pb dating of preserved magmatic zircon cores yielded mean concordant 206 Pb/ 238 U ages of 456.7 \pm 5 Ma and 462 \pm 4/-7 Ma, respectively (Fig. 2).

Detrital zircons in the gneissic metasedimentary host rock display a large age range from Achaean rounded grains (3.5 Ga for the oldest) to Cambrian-Ordovician prismatic grains (550 to 475 Ma). As the youngest detrital zircon (456 \pm 9 Ma) and the intruding gabbros have the same age within errors, deposition of the volcanic-detrital sequence occurred in a short time span. The mafic volcanic component in the sediments is also very close in composition to the gabbro intrusions and thus seems linked to the same magmatic event.

The Metailler Formation is interpreted as a sedimentary basin infill with a continental input documented by Achaean detrital zircons, located close to a mafic volcanic centre. The sedimentary context and the magma compositions are consistent with a back-arc environment. According to geodynamic reconstructions (e.g. Stampfli et al. 2011), the future Middle Penninic domain was part of the north-Gondwanan active margin at that time, which was progressively drifting off main Gondwana in response to the southward subduction of a northern oceanic domain. Thus the Ordovician Métailler Basin might document the early back-arc opening of north-Gondwana which ultimately gave birth to the eastern Rheic ocean.



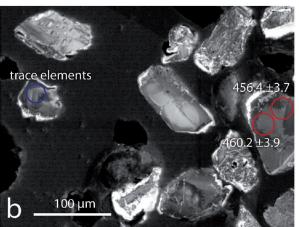


Figure 1. a) Banded gabbro body; b) Zircons of an albitic dikelet (epoxy mount, cathodoluminescence image, circles are LA-ICPMS (25µm) analysis spots.

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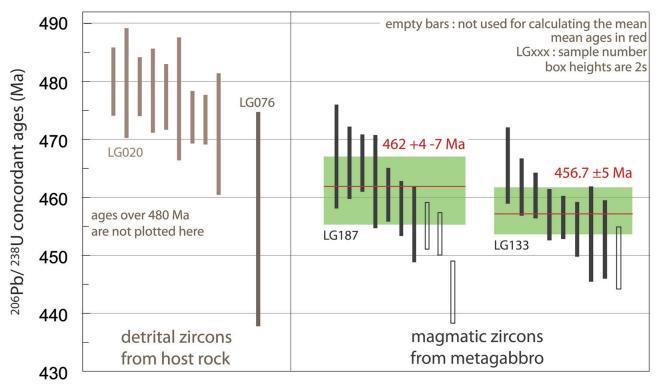


Figure 2. Summary of LA-ICPMS concordant ²⁰⁶Pb/²³⁸U zircon ages.

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Geochemistry of Paleocene-Eocene limestones from Ching-dar syncline, west of Birjand, east of Iran

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The Ching-dar syncline area is located in the east of Iran belt (after Alavi, 1991) (fig. 1). The studied sequence is about 500 m in thickness and consists of both skeletal and non-skeletal grains e.g. foraminifera, green algae, peloids, and intraclasts. They were deposited in a shallow marine carbonate ramp. The studied limestones were subjected to extensive diagenetic processes with varying intensities, the most important of which are cementation, compaction (mechanical and chemical), internal filling and stylolitization. Chemical analysis of the limestone samples revealed high calcium and low magnesium content.

Major and minor elements values were used to determine the original carbonate mineralogy of the Ching-dar limestones. Petrographic evidences and elemental analysis indicated that calcite was the original carbonate mineral in the Ching-dar limestones. The amounts of Mn and Sr/Na ratio in the studied samples, compared to the sub-polar cold-water Permian limestone, sub-tropical warm-water Ordovician aragonite (Rao, 1990, 1991), recent tropical shallow-marine aragonite (Milliman, 1974) and recent temperate bulk carbonate (Rao & Adabi, 1992; Rao & Jayawardane, 1994; Rao & Amini, 1995) indicate original carbonate mineralogy.

The elemental compositions of the Ching-dar carbonates also illustrate that they have been stabilized in a meteoric-phreatic diagenetic environment. Variations of Sr/Ca ratio versus Mn suggest that diagenetic alteration has occurred in an open system.

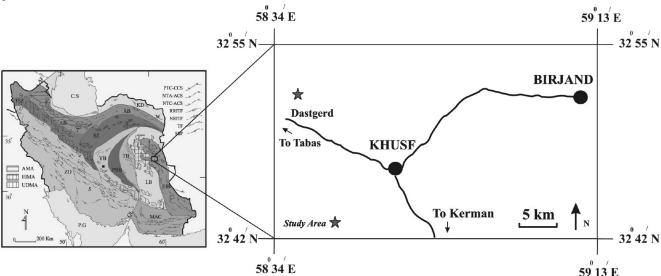


Fig 1. Left: Generalized tectonic map of Iran (after Alavi, 1991), EIB-east of Iran belt. Right: simplified location map of the studied area.

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New age constraints on the opening of the Piemont-Ligurian Ocean (Tasna-Nauders area, CH-A)

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The Engadine Window in Eastern Switzerland/Western Austria exposes the Lower-Middle Penninic Tasna nappe, which was recognized to preserve a pre-alpine Ocean-Continent-Transition (OCT) by Florineth (1994) and Florineth & Froitzheim (1994) in the Piz Minschun area. The present study confirms the observed OCT geometry in a more eastern part of the Tasna nappe at the border between Switzerland and Austria: Mapping of the area SW of Nauders reveals the contact between serpentinized spinel-lherzolites and NE-ward out-wedging upper-continental crust which is sealed by a continuous layer of sediments. Compilation of geological maps of the South-Western part of the Window allows lateral connection of the newly mapped Nauders-OCT with the Tasna-OCT of Florineth (1994) around the border of the Window. The obtained overall geometry shows an approximately 8km long extensional allochthonous block comprising pre-, syn- and post rift sediments in normal position whose northern-, eastern- and southern border can be delimited. The lateral width of this block is undefined because it disappears beneath the Austroalpine nappes in the West.

Petrologic and geochemical investigations on serpentinites and (former-) garnet-pyroxenites confirm the subcontinental origin of the Tasna mantle and allow constraining its evolution. Pyroxenites formed at depths of at least 45km as indicated by the presence of garnet pyroxenites. Garnet subsequently almost completely decomposed to spl-opx-cpx symplectites by reaction with olivine in the spinel stability field at temperatures of initially ~830-950°C and shallower depth of 30-45km.

This corresponds to an uplift of the mantle rocks below a thinned continental crust and can possibly be linked with the late Carboniferous-Permian extension event. Almost complete decomposition of garnet associated with recrystallization and beginning equilibration of primary pyroxenes indicates relatively long residence at this sub-crustal depth during which the rocks cooled. The last event recorded in the mantle before exhumation is percolation of a K-rich Ca-poor alkaline liquid leading to formation of phlogopite and zircon in small, local veins. This event represents the rise of the first, unambiguous rift-related magmatic liquids in the area. Age determination on such a vein yields U-Pb ICP-MS crystallisation age of 167.3±2.7Ma for zircon and an Ar-Ar age of 167.55±0.9 Ma and 167.9±1.4 Ma for phlogopite, these ages are identical to the Ar-Ar phlogopite age of 170.5±0.4Ma and 169.1±0.4Ma obtained for the Tasna mantle (Manatschal et al. 2006).

These ages indicate Middle-Jurassic magmatism for low-degree mantle melts and are consistent with ages known for the South Penninic Piemont-Ligurian Ocean. They argue against a lower Cretaceous rifting of the NE part of the Valais domain and confirm the South Penninc origin of the Nauders-Tasna nappe already proposed by Manatschal et al. (2006).

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Origin and Paleotectonic Conditions of Formation of Ore-Containing Fractures of the Lichk-Aygedzor Ore Field of Southern Armenia, Lesser Caucasus

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The Lichk-Aygedzor ore field lies in the central part of the Megri composite pluton in Southern Armenia, between Kadjaran in the north and Agarak in the south. As opposed to the adjacent blocks, where large reserves of copper-molybdenum deposits are concentrated (Kadjaran, Agarak), the Lichk-Aygedzor block is distinguished by a spatial coincidence of deposits with average reserves of copper-molybdenum and gold-sulphide formations. They are: Terterasar, Tey, Lichkvaz gold-sulphide and Lichk, Aygedzor copper-molybdenic deposits.

The composite Meghri pluton consists of a broad spectrum of intrusive rocks of Upper Eocene-Lower Oligocene age, including olivine gabbro, monzonite, syenogranite, granodiorite, as well as porphyritic granite-granodiorite of Lower Miocene age (Melkonyan et al. 2008).

The controls of the ore deposits and prospects of the ore district are attributed by Hovakimyan &Tayan (2008) to circum-latitudinal and northeastern-oriented discontinuous fractures, particularly, the intersection with east-west-oriented fractures.

On the basis of our knowledge about the formation mechanism of fractures under shearing conditions (Sylvester 1988 and others), we made an effort to analyze the possible shifts of blocks during ore formation.

The investigated deposits were controlled by the above-mentioned circum-north-south-oriented fractures and the intersection with other fracture systems, particularly, circum-latitudinal and north-eastern extensions. The right-shearing displacements by the ore-controlling fractures analyzed on block-diagrams (Hovakimyan & Tayan 2008) contributed to open of northeastern-oriented fractures, containing copper-molybdenum and gold-sulphide mineralization. It is important to take into account the latter circumstance during projection of the numerous ore prospects and it can significantly contribute to the productivity of geological prospecting programs.

With the aim of reconstruction of the plan of deformation and spatial orientation of the axes of paleo-stresses (Gzovskiy 1975), during field work, we defined adjoint systems of spalling cracks, measured the orientation of lineations along fracture planes, which underwent shearing displacements. We also used the maximum data of circular crack diagrams.

For the axes of stresses, according to Gzovskiy (1975), we used the notation of axis of compression and extension- σ 3 and σ 1, respectively. The intermediate axis being σ 2, whereby σ 3 \geq σ 2 \geq σ 1.

Based on our results, the compressive forces were oriented along southwest and northeast directions and contributed to the spatial orientation of the axes of paleo-stresses and formation of tectonic fracturing of the Lichk-Aygedzor ore field. The axes of compression were oriented towards the horizon under average angles of 30-35°.

The dynamic conditions produced by stresses oriented northeast-southwest were favorable for the right shearing displacements by the plates of circum-meridional ore-controlling fractures with development (renewal) in the ore stage of northeastern oriented ore-containing systems of cracks undergoing opening. Their orientation parallel to regional northeastern-southwestern compression and circum-horizontal location of axis of elongation, transverse to ore-containing fractures contributed to the conditions of extension.

The same direction of paleo-stresses together with the general orientation of axis of the north-south compression was obtained during recent regional investigations (Avagyan et al. 2005), and was related to the movement of secondary blocks during Arabian - Eurasian convergence.

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The influence of bulk and mineral ferric/ferrous ratios on thermobarometry of the Syros/Sifnos blueschists: Towards a new thermodynamic model for high pressure amphiboles

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Blueschists are a key source of information regarding the thermo-mechanical evolution in subduction zones. They record temperature and pressure conditions of rock material transported down to great depths along the slab. The involved processes cannot be studied in situ so that investigations rely on recalculations and modeling based on thermodynamic properties of minerals. Current models based on charge balance may be inaccurate. In particular, elemental site occupations can vary dramatically in sodic amphiboles, which have a complex structure. Little is known on the ferric/ferrous iron ratio in glaucophane although it has been argued that changes in bulk or mineral values may have a drastic impact on the stability field of these minerals. To constrain our knowledge on subduction processes and the minerals defining the blueschist facies, we need to rely on realistic values. Otherwise, we might misestimate pressure and temperature conditions required to form such rocks.

Samples of varying pressure/temperature conditions and mineral parageneses have been selected in order to get a more general understanding on iron distribution under distinct conditions. Photometry is used to measure ferrous iron in both bulk and mineral compositions. For the mineral standards this values will be crosschecked with Moessbauer spectroscopy. Further measurements have been made with micro-XANES, which has the great advantage of in situ spot analyzes allowing to measure zoning in single crystals or contact zones within the original texture.

We present new data of bulk and mineral analyses of different types of blueschists focusing on samples from Syros and Sifnos (Cyclades, Greece). We chose these rocks because they contain garnet and white mica, which allow common thermobarometric estimations, thus some sort of calibration. Besides, the sodic amphiboles are fresh and chemically unzoned, which is crucial for using methods based on whole grain analyses. We found bulk and mineral ferric iron values higher than most charge balance recalculations yield. This result comforts the certainty that it is fundamental to incorporate measurements to ensure optimal results. The influence of measured ferric/ferrous iron contents on the thermobarometry of the Syros/Sifnos blueschists is discussed along with the potential for new constraints on amphiboles regarding recalculations of metamorphic conditions.

P 2.12

X-ray diffraction and thermal analyses of a bangle shard from an Indus valley settlement

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In Pakistan, Harrappa is recognized as one of the most important and magnificent site of the Indus Valley Culture that flourished around 2600 BCE in this region. In order to determine the type of contents used in making bangles in Harrappa, a specimen shard was tested using the facilities available in Geoscience Advance Research Laboratories in Islamabad. The mineralogical make up of the clay used in the bangle shard was determined using XRD analysis while simultaneous TG/DT analyses were carried out to establish thermal properties and nature of phase changes that took place while the bangle was processed.

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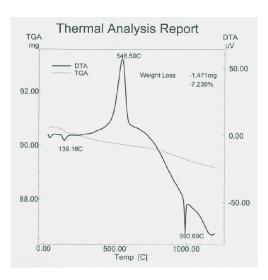


Figure 1. Results of simultaneous TG/DT analyses.

XRD analysis shows that the mineralogical make up of the clay used in the bangle shard includes montmorillonite $((Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O)$, gypsum $(CaSO_4 \cdot 2H_2O)$, and quartz (SiO_2) . Results of thermal analysis have been included in the contract of the ded in Figure 1. The temperature was varied in steps of 20°C/min from room temperature to 1200°C. For a sample mass of 20.32 mg, a loss of 1.471 mg or 7.239% was observed. There is a regular trend in mass loss over the entire heating range, which shows that the clay or clays used in the bangle shard are almost uniform in composition and properties. Mass loss in clays during thermogravimetric analysis can be divided into three stages: dehydration from room temperature to about 200°C, decomposition of hydroxyls from 400°C to 650°C, and decomposition of carbonates in the range 700-800°C (Drebushchak et al. 2005). The TGA curve for the specimen shows mass loss occurring in three distinct steps. The initial mass loss (0.15 mg) attributed to dehydration is very small, but it coincides with an endothermic peak at 139.16°C on DTA curve. (An endothermic effect attributed to presence of gypsum is also observed in the range 100-120°C (Moropoulou et al. 1995).) From this temperature onwards there is a gradual mass loss of 0.75 mg up till 850°C. Finally a mass loss of 0.5 mg is recorded from 850°C to 1200°C on the last portion of TGA curve. The mass loss around 400-650°C which coincides with a sharp exothermic peak at 546.5°C on DTA curve can be attributed to combustion of organic material in the tested specimen (Moropoulou et al. 1995). This organic material may have been added by ancient potters as a binder. (From XRD analysis, abundance of montmorillonite and the characteristic two endothermic peaks on DTA curve provide the evidence that the major constituent of the tested specimen is bentonite. The thermal analysis curves for the tested specimen can be compared with modern industrial bentonite (from India) and the trends are almost similar (Venkatathri 2006). A difference (in peaks and ranges) may exist due to addition of other components in the raw ceramic material of the bangle shard specimen.) Studies have shown that montmorillonite is destroyed when fired to a temperature of 860°C (Drebushchak et al. 2005). If montmorillonite has survived the firing stage during processing of the bangle, it appears that the temperature in the firing kiln was not in excess of 860°C.

Quartz has also been detected in XRD analysis. It is a non-plastic material where as bentonite is known to be very plastic and suited for complex shapes. Quartz may have been added in the raw ceramic material as a temper to allow water to evaporate smoothly (thus avoiding cracking) and also to improve handling and working of the raw clay. But unknown to ancient potters of Harrappa, this addition may have caused the bangles made out of this raw material to become less resistant to mechanical stresses while in use. An endothermic effect is observed from 600-950°C. There is a sharp endothermic peak at 993.69°C followed by an exothermic effect at about 1020°C. The endothermic effect especially around 800-950°C can be attributed to decomposition of any carbonates in the raw ceramic material used for making this particular bangle. No amount of calcite or dolomite has been identified in XRD analysis (given the limitation of the XRD apparatus not being able to detect minerals less than 10 wt% of the sample), the most usual carbonates in ancient ceramic materials (Moropoulou et al. 1995). The endothermic peak at 993.69°C can be interpreted as an indication of appearance of a crystalline phase (i.e. due to vitrification of quartz) in the sample (above 800°C), which might have undergone a solid-phase polymorphic transformation at this high temperature (Krapukaityte et al. 2008; Moropoulou et al. 1995).

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Petrographic and sedimentologic investigations of boulders of the river Wiese (southern Baden-Württemberg, FRG)

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The river Wiese has its source in the southern Schwarzwald (south Germany) and carries a prominent amount of clastic material to the river Rhine. A petrographic and sedimentologic investigation on aims to elucidate the changes in composition and maturity of boulders along the course of the Wiese river and its final supply to the Rhine river. At 5 sampling sites representative material was collected.

The first sampling station is located in the upper reach of the river Wiese, about 6 km downriver of its source at the Feldberg. High-grade metamorphic rocks (migmatitic gneisses) represent the largest proportion of the boulder population whereas fine to medium grained granites are subordinate. The gneisses, which crop out in the whole Feldberg area of the southern Schwarzwald, are mainly metapelitic types with prominent biotite, sillimanite, garnet, plagioclase, K-feldspar and quartz. The granites are mostly fine-grained and partly medium-grained. They are probably derived from smaller dykes and sills cutting through the metamorphic Variscan basement. The boulders from this site are moderately rounded.

The second sampling site is located north of the village Hausen, about 20 km downriver of the first site. It is situated at the boundary between the Schwarzwald and the Dinkelberg Block where Triassic sedimentary rocks crop out. Besides basement gneisses and porphyric granites, bioclastic limestones and sandstones form part of the boulder spectrum. Due to local erosion, the limestones form angular boulders, whereas the sandstones are well-rounded and relatively small while brought in by a tributary creek (Fig. 1). Intriguing is the occurrence of basaltic components probably delivered from the Badenweiler-Lenzkirch-Zone. The Wiese passes this Permo-Carboniferous structure a few kilometers upstream from this location. In addition, quartz porphyrites, conglomerates and subordinate quartzites are derived from this zone.

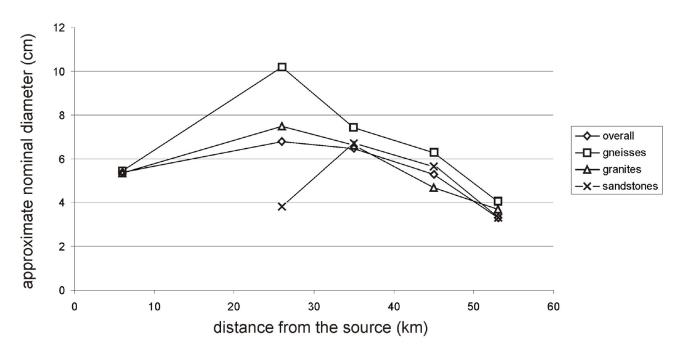


Figure 1: Diagram showing variation of approximate nominal diameter of boulders with distance

The third sampling site is located another 9 km downstream from Hausen at a retaining barrage near Maulburg. The boulders exhibit a wide variety in composition including basement gneisses, granites, porphyrites, basalts and Upper Permian sandstones. The amount of the latter is significantly enlarged as the Wiese actively erodes a cliff. Apart from the sandstones, the grain size of the boulders is decreasing (Fig. 1).

The fourth sampling location is at a retaining dam in Lörrach-Tumringen, which is another 10 km downstream from Maulburg. The lithology of boulders does not change but the proportion of Triassic rocks, in particular sandstone, markedly increases. Grain size decreases (Fig. 1) and roundness increases for all lithologies.

The last sampling station is an abandoned grave pit in Weil am Rhein, about 53 km downstream from the source of the Wiese river and close to the Rhine river. Here, a mixture of material derived from the Wiese catchment area, the Jura Mountains and the Alps occurs. For the first time, greenish granites showing a low-grade metamorphic overprint, are present. Furthermore, we observe fine grained amphibolites, radiolarites, flysch sandstones and quartzites from the Alps occur. The Jura Mountains delivered considerable amounts of greyish micritic limestones. Thus, the proportion of Wiese material is low. All the pebbles are fine-grained (Fig. 1) and quite well rounded.

A further quantification of textural and compositional data will be carried out.

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P 2.14

Element partitioning between immiscible carbonatite- and silicate melts from 1-3 GPa

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The goal of this experimental study is to determine element partition coefficients ($K_{\rm D}^i$) between conjugate and immiscible carbonatite and silicate melt pairs at pressures of 1-3 GPa in H₂O-free and H₂O-bearing systems. The determined $K_{\rm D}^i$ -values quantify the element partitioning between immiscible silicate-carbonatite melts and provide a tool to test for liquid immiscibility of natural melts from volcanoes erupting both silicate and carbonatite magmas.

Partition coefficients were determined for 3 water-free and 4 water-bearing systems with different silica contents between 1-3 GPa and 1150-1260°C. In the water-bearing experiments, the physical separation of the immiscible melts was sufficient to determine the partition coefficients. Major elements were analysed by electron probe microanalysis and trace elements by LA-ICP-MS for >40 elements. For the water-free systems, centrifugation at 700 g, at identical PT conditions as in the equilibrium experiments, was necessary to segregate the coexisting liquids in order to analyse them.

The partition coefficients of the dry systems are within a range of factor 4 for most elements. The alkali and alkali earth elements partition into the carbonatite melt as well as P and Mo, whereas the HFSE and most transition metals have a stronger affinity for the silicate melt. The LREE elements partition weakly into the carbonatite melt whereas the HREE prefer the silicate melt ($K_{\rm D}^{La}/K_{\rm D}^{Lu}$) = 1.6 to 2.3).

For the water-bearing systems, the addition of water increased the width of the immiscibility gap, resulting in higher partition coefficients. The highest partition coefficients for Ca and the LREE (>30) were obtained in silica-rich water-bearing systems.

The alkali-rich compositions of carbonatite melts in our as well as previous studies indicate that primary carbonatites, which are immiscible with silicate melts, ought to be alkali-rich. As both, low degree of melting or fractionation of CO₂-rich melts (the two other mechanisms) also lead to alkali-enrichment in the carbonatites, we propose that pure calcite or dolomite carbonatites do not represent true liquid compositions. Nevertheless, we are not questioning the igneous characters of such calcio-carbonatites, but assume that these are primary cumulates or altered through weathering processes. It is likely that most carbonatites have lost at least part of their initial alkali-contents by leaching through magmatic- or meteoric fluids.

The Petrology and Geochemistry of the Civrari-Southern Lanzo Ophiolite, Piemonte, Western Italian Alps

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Alpine-Apennine ophiolites have been found to represent subcontinental lithosphere emplaced at ocean-continent transition zones during lithospheric thinning and exhumation during the opening of the Alpine Tethys in Jurassic times [1,2]. Preserved mantle rocks have provided insight into mantle dynamics occurring at different depths, from melt-rock reaction and asthenospherization to melt intrusion. The presence of a small outcrop of peridotites within a sliver of slow-spreading oceanic crust, represented by the Civrari Ophiolite [3], has given us the ability to study peridotites and magmatism in a more oceanward environment. The Civrari peridotite consists of a small lense of both refractory and reactive lherzolites intruded by late stage low-pressure olivine-gabbros. The ultramafic massif in itself is strongly homogeneous and of refractory nature, with strongly contrasting compositions when compared to subcontinental mantle exhumed throughout the Alps. A detailed study suggests that the Civrari peridotite originated from a deeper part than the Lanzo peridotites, with preserved high temperatures (1200-1300°C) suggesting rapid exhumation to the ocean floor, without any prior accretion to the subcontinental lithosphere. These peridotites were formed through ~13% partial melting, beginning in the stability field of garnet, before reaching the spinel stability field. Localised percolation of small melt increments (very low melt/ rock ratio) in the stability field of spinel caused some areas of the Civrari peridotite to become reactive lherzolites (dissolution of orthopyroxene, precipitation of ol + spl + cpx), before localised melt impregnation at shallower lithospheric levels dissolved clinopyroxene to form orthopyroxene + plagioclase. Preserved reacted clinopyroxene show trends of LREE, TiO, and Na,O enrichment, with core to border zonations. Impregnation of lithospheric peridotites by orthopyroxene-saturated melts is consistent with migrating melts cooling and crystallizing during the exhumation of the peridotite. MORBtype aggregated magmas between the Civrari and Southern Lanzo domains intruded around 150 Ma as shown by plagioclase-clinopyroxene Nd mineral isochrons, and originated from a similar MORB-type depleted asthenospheric source. Increase in partial melting by the Civrari Ophiolite, coupled with the high temperatures recorded in peridotites, and the limited melt-interaction suggests that the Civrari ophiolite is found in a more oceanward environment than the Southern Lanzo peridotite, and might represent Jurassic-age oceanic crust.

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CRIME SCENE INVESTIGATION AND FORENSIC MINERALOGY APPLICATIONS AT GURPINAR (ISTANBUL – TURKEY) MURDER

GURPINAR (ISTANBUL – TURKEY) CİNAYETİNDE OLAY YERİ İNCELEMESİ VE ADLİ MİNERALOJİ UYGULAMALARI

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A reliable CSI is the most important step of Forensic Investigation to find out the crime and cirminal. It is a fundamental legal principle to reach guilty from evidence and to judge the accused with the legally obtained evidence. In the recent years, using multidisciplanary studies are increased in Forensic Science by the development of science and technology. Compiling bioligical samples, finger prints researches, forensic materials is important to solve the crime, to ensure the justice and to relief.

The scope of this study is to highlight the using of forensic mineralogy and crime scene investigations in forensic science. Fort his purpose, the mineralogical findings were compared. The mineralogical findings were collected from crime scene and from a buried 50-55 aged male body found on the sea cost of Büyükçekmece Gürpınar. Also some of the findings were taken from the houses and cars of suspects who can be related to the crime.

ÖZET

Suç ve suçlunun ortaya çıkarılması için yapılan soruşturmanın en önemli ayağını iyi yapılacak bir olay yeri incelemesi oluşturmaktadır. Delilden sanığa ulaşmak ve sanığın yasal olarak elde edilecek delillere dayanılarak yargılanması temel bir hukuk prensibidir. Son yıllarda teknoloji ve bilimin gelişmesine bağlı olarak adli olayların çözümünde multi-disipliner çalışmaların kullanımı artmaktadır. Olay yerinde biyolojik örneklerin derlenmesi, parmak izi araştırmaları, adli mineralojik materyallerin toplanması vb. uygulamaların tümü olayın aydınlatılması, adaletin sağlıklı bir şekilde uygulanması ve mağduriyetlerin giderilmesi için önem arz etmektedir.

Bu çalışmada; adli mineralojinin adli bilimler alanında kullanımı ve olay yeri incelemesindeki öneminin anlatılması amacı ile Büyükçekmece Gürpınar sahilde toprağa gömülü vaziyette bulunan 50 – 55 yaşlarındaki erkek cesedinde olay yeri ve otopsi sırasında toplanan mineraloji materyal ile ve olayla ilgisi olduğu düşünülen şüphelilerin ev, olayda kullanıldığı düşünülen arabalarının olay yeri ekiplerince yapılan incelemeleri sonucunda elde edilen bulguların karşılatırılması anlatılmıştır.

P 2.17

Geochemistry and petrogenesis of the Dehsheikh Peridotitic Massif (South of Iran)

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Peridotitic tectonites from the Dehsheikh Massif record a spinel-peridotite facies condition, and indicated by deformation from tectonite to mylonitic fabrics in south of Iran. The ophiolitic peridotites are considered to represent by residual mantle that was tectonically formed by rifting and opening of the Jurassic Neo-Tethys embryonic ocean in fore-arc tectonic environment.

These peridotites include spinel-harzburgites and dunits, which display overall depleted geochemical signature.

Peridotites from the Dehshekh Massif are very refractory with low modal clino-pyroxenes, chrome-rich spinels with Cr# = 0.6 – 0.9 and Mg# = 0.4 – 0.6. Also, these samples show U-shaped rare earth element (REEs) profiles demonstrated that these peridotites have undergone extensive interaction with LREE-enriched subduction-derived fluids and depleted mantle residues.

Harzburgites and dunits are considerably characterized by more oxidized features, with calculated oxygen fugacities between FMQ +1 and FMQ +1.5, in comparison to other subduction zone related peridotites. Fractional melting modeling indicates that these peridotite samples are derived by 25-30 % melting of mantle in a supra-subduction zone environment.

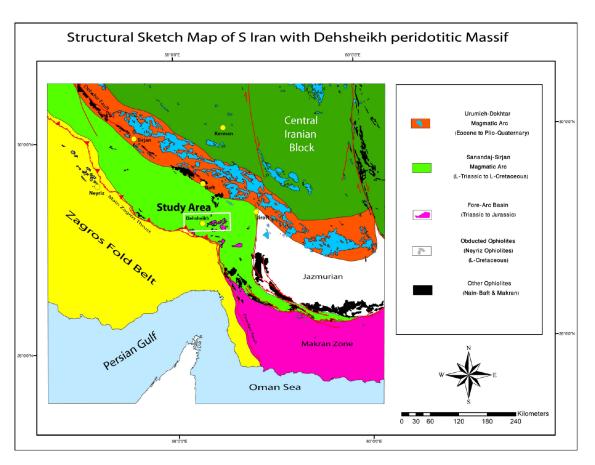


Figure 1. Simplified structural sketch map of Dehsheikh Peridotitic Massif in south of Iran. The location of study area with major structural zones consisting of Sanandaj-Sirjan Magmatic Arc, Central Iranian Block, Urumiyeh-Dokhtar Magmatic Arc, Makran Zone and Zagros Folded Belt are indicated.

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Sr, Nd, and Pb isotopic constraints on the origin of the central Iran linear volcanic chains

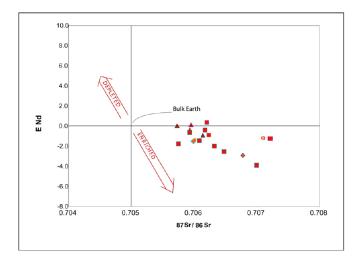
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The Miocene linear volvanic activity in the northwestern part of Iran is considered to be extensional basins after the Arabian – Eurasia collision. The samples are mainly andesitic basalt to andesite and were analyzed according to Nd-Sr-Pb isotopic compositions in order to understand the petrogenetic signature of volcanic rocks. The magmatism at these regions are calc-alkaline in affinity.

The analyzed samples are characterized by ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios (0.7056 to 0.7071), Epsilon Nd values (0 to -3.5) and ${}^{143}\text{Nd}/{}^{144}\text{Nd}$ (0.51246 to 0.51267) which indicate contribution of a mantle component in origin. The Pb isotope evidence is particularly high with ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ ratios (38.731 to 39.097), ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ = 18.770 to 19.004 and ${}^{207}\text{Pb}/{}^{204}\text{Pb}$ = 15.645 to 15.706.

This observation from the isotopic evidence for the volcanic chain implies that they probably originated from melting of enriched-mantle source, which ascribed to oceanic sediment played a major role in the origin of the volcanic rocks. The isotopic data suggest that the parent magma underwent fractional crystallization and were contaminated by crustal rocks similar to that of the lower crust.



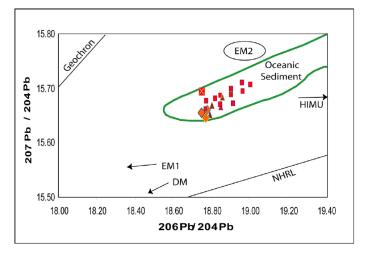


Figure 1. plot of Epsilon Nd versus 87Sr/86Sr ratios. Plot of 206Pb/204Pb versus 207Pb/204Pb ratios. NHRL (Hart, 1984).

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P 2.19

Na-bearing garnets with oriented lamellar inclusions – are those majorite precursors? A case study from the Rhodope Massif (Greece)

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The Rhodope Massif in northern Greece – southern Bulgaria is an Alpine synmetamorphic nappe complex. The presence of microdiamonds as inclusions in metamorphic minerals of the intermediate thrust sheets is taken as evidence of ultrahigh-pressure metamorphism (UHPM – P > 2.5GPa). One of the major UHP mineral indicators is garnet with lamellar inclusions of clinopyroxene, rutile \pm apatite. Such lamellae are interpreted as the result of exsolving processes during decompression and cooling of majoritic garnet from UHP conditions.

We investigated an eclogite from the diamond-bearing tectonic unit in eastern Rhodope. The main mineral assemblage is grossular-almandine-rich garnet, omphacite, quartz, plagioclase, amphibole, clinozoisite, epidote and calcite; rutile, titanite, ilmenite and apatite are accessory phases. Omphacite and plagioclase form symplectites in the rock matrix. Garnets are zoned with respect to their manganese and sodium content whereas magnesium, calcium and iron are homogeneously distributed.

The chemical zoning in manganese is consistent with a fractional crystallization model and the sodium zoning follows the same trend. The mechanism responsible for the incorporation of sodium in garnet is the substitution MgAl=NaTi. Conventional thermometry using garnet-clinopyroxene pairs at the rim of the garnet yield temperatures of 650° C ($\pm 75^{\circ}$ C).

All of the garnet grains exhibit lamellar inclusions of titanite, quartz and rutile which are oriented systematically within the crystal lattice of the garnet. Electron backscattered diffraction (EBSD) revealed that the lattice preferred orientation of these lamellar inclusions is not related to the lattice orientation of of the host garnet. This crystalline relationship does not support an exsolution-type origin of the oriented lamellar inclusions, which would also require higher temperatures than that calculated.

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Investigations of fluid inclusions in quartz crystals in the dolomitic rocks of the Binn-Valley, Switzerland

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The aim of our investigations is a comparison of several sulfosalt bearing mineral localities in dolomitic rocks of the Binn-Valley (Wallis, CH), in terms of their mineralizing fluids. So it should be possible to improve the knowledge about the formation of the Lengenbach deposit. The Lengenbach quarry is one of the most famous mineral collecting sites in Switzerland. In the last decades, numerous investigations on geology, mineralogy and ore formation for this mineralization were done. The richness of sulfosalt minerals and the occurence of Tl-sulfosalts is of specific scientific interest. The mineral deposit is located in Triassic meta-dolomites, underlayed by Jurassic schists (Bündnerschiefer). Over the dolomitic rocks different Pretriassic ortho- and paragneises occoure(Hügi 1988). Due to the tectonic settings the primary stratigraphic sequence of the rocks is reversed. Beside the Lengenbach quarry, other sulfosalt bearing deposits are known, situated within dolomitic rocks. The most famous are Reckibach, Turtschi and Messerbach. Especially the localities Reckibach and Turtschi show considerable differences in their element dominances refered to the sulfosalt- and sulfide minerals. The outcrop Turtschi shows a Sb-Bi-dominance whereas Reckibach is clearly Ag-dominated. The Lengenbach quarry in addition is characterized by the occurence of Tl-sulfosalts and shows the largest mineral diversity of all outcrops (Graeser 1965). Quartz crystals from fissures and cavities are the hostmineral of the investigated fluid inclusions. A differentiated inclusion petrography and microthermometric investigations are the basis of this work. It enables to evaluate the approximated composition and density of the mineralizing fluid. Daugther minerals, like halite, calcite and sphalerite were analyzed by Raman spectroscopy.

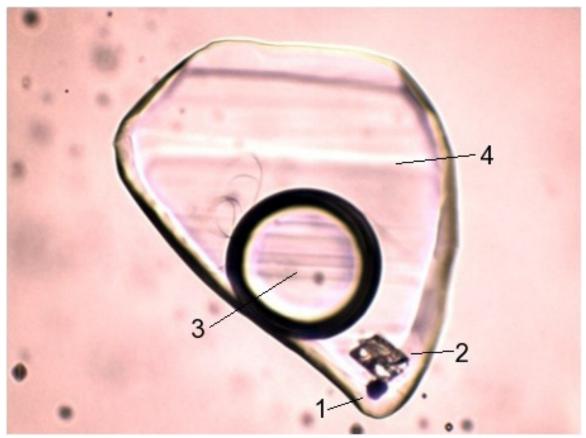


Figure 1. Fluid inclusion (180 μ m) from the location Tschampigen Wyssi, 1: sphalerite, 2: calcite, 3: CO $_2$ (liq.), 4: aqueous solution

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Stratigraphic successions in the Avers unit, southern Grisons, and comparison with the Tsaté unit, W Alps

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The Avers schists are known as a complex of Mesozoic sediments with some ophiolitic rocks since the pioneering work of Rudolf Staub (1926). At that time serpentinites and basic rocks were attributed to lit-par-lit or sheet-like intrusions into basinal sediments in Cretaceous times. This mechanism fits at first sight with the map view, because ophiolitic rocks can be traced as narrow layers, including possible volcaniclastic deposits, over some distance. The abundance of ophiolites in the Avers unit increases towards the South. Staub also mapped in detail the overlying tectonic unit, the Platta ophiolites, that consist mainly of serpentinite, gabbro, pillow lava to greenschist and of associated sediments, namely thin layers of metaradiolarite (banded quartz schist) and bright marble.

The question remained whether the Avers ophiolites are sill-like intrusions or not. Field work in the southern part of the Avers unit (1977-1982) revealed wide spread occurrence of thin layers of metaradiolarite, sometimes with manganese mineralisation, and bright marble. Often associated with serpentinite lenses, the succession in the field is greenschist – metaradiolarite with Mn - bright marble – grey limestone/calcschist. This succession, reported here for the first time from the Avers unit, is similar to that from ophiolitic rocks in the Appennines, W Alps, the Platta nappe and to the stratigraphy in the Austroalpine Margna and Err nappes. Sediments associated with Avers greenschists are therefore correlated with the sequence also known as radiolarite (banded chert + Mn) - calpionella limestone - argille a palombini/Emmat-Fm (middle Jurassic - Early Cretaceous).

The distribution of ophiolitic rocks in the Avers schists is therefore mainly due to tectonic imbrication with other sedimentary series. The lower part of the Avers unit overlies Triassic quartzites and dolomite/calcite marbles of the Suretta nappe and consists mainly of carbonate sediments with some detrital layers. The breccias contain Triassic carbonates and indicate the break up of an adjacent platform. Sandstones and "silty green schists" made up of chlorite, some quartz and muscovite (and can be confused with basic greenschist in the field), partly represent material from the Roffna porphyry (basement of the Suretta nappe).

In the upper part of the Avers unit a stratigraphic succession can be mapped in areas with continuous outcrops. Age and stratigraphic younging is not verified, but comparison with the série grise and série rousse from the Tsaté nappe (Marthaler, 1984) suggest Early to Late Cretaceous and the following sequence of formations. (Instead of correct rock names in greenschist facies, e.g. calcschist, grey phyllite, Peters and Dietrich (2008), the terms for unmetamorphic rocks are used for description). The lower (?) series of alternating limestones and dark mudstones typically contain detrital layers of sandstones, siltstones, fine to medium grained (mm to cm) breccias with clasts from various dolomite and limestone source rocks (Triassic, Liassic....?). More visible in the field are 0.1 to 3 m thick layers of bright dolomite and dolomite-limestone breccias. The following dark "shaly" formation of black to grey siltstones and mudstones is 1-2 m thick. The overlying quartz-rich sandstone formation reaches 10 m. These mudstones and sandstones could represent rocks from the mid Cretaceous. The overlying formation can reach over 50 m and builds up Piz Piot. Alternating marly limestones and marls/ mudstones without detrital layers are typical. This series is correlated with the série rousse of Marthaler (1984) and would then represent the Late Cretaceous. Towards the upper eastern tectonic boundary of the Avers unit another sandstone formation and a mappable "sandstone-rich tectonite formation" below the Turba mylonite zone can be distinguished.

Comparison of the Avers schists with rocks in the Tsaté nappe (Combin zone, below the Dent Blanche nappe in the Western Alps) revealed identical rock successions at very similar grade of deformation and metamorphism. Metaradiolarites, typically banded quartz schists with Mn mineralisations, are widespread and associated with many greenschists, from Val de Zinal, Val de Moiry, Val d'Arolla to Val de Bagnes S of lac de Mauvoisin. West and east of lac de Moiry the rocks are easily accessible along N-S trending crests. Thin metaradiolarite and marble layers (0.1 - 2 m) are generally still attached to greenschists, some are recognisable as former pillow lava. Packages of "argille a palombini", dismembered from the original sequence, are prominent W of lac de Moiry, where also the série grise and rousse can be studied. Towards Pointe du Tsaté sandstones prevail in the upper part of the Tsaté unit. "Many rocks in the Avers unit" are therefore to be studied more easily in the lac de Moiry area.

The Avers and Tsaté units are very similar and are interpreted as accretionary wedges rich in sediments containing some oceanic rocks. They are known from many places in the Alpine chain. These units are distinguished from ophiolite-rich (sediment-poor) units such as the Platta nappe, Zermatt-Saas zone etc.

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P 2.22

Minor and trace elements controlling the visible and near-infrared light transmittance of wolframite, pyrite and enargite

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In the ore deposit research, fluid inclusion studies can be conducted on ore minerals which are transparent to visible or near infrared radiations (Campbell and Robinson-Cook, 1987). The light transmittance of these semi-conducting minerals depends on the width of the band gap energy in their electronic configuration (Campbell 1984): if an incident light going through the mineral structure has an energy larger than its band gap energy, the light will be absorbed and the mineral will be opaque. Low-energy radiation (infra-red light, IR) is therefore used for transmitted light microscopy to observe internal features in minerals that are usually opaque to the visible light.

In this communication, we discuss the effect of minor and trace element content of wolframite, pyrite and enargite on the mineral transmittance to better assess the limits of visible and IR light ore microscopy.

Image analysis using the gray scale value (GSV) of visible and NIR transmitted-light photomicrographs allows having a rapid rough estimation of the mineral transmittance. Further analyses with FTIR micro-spectroscopy will quantify the IR transmittance of the following minerals as a function of the wavelength in the interval 1.0-3.0 mm.

The selected hübnerite crystals, Mn-rich wolframite from the Toromocho deposit in central Peru, are transparent to visible light and have growth zoning that has been investigated by electron microprobe (EMP) and LA-ICP-MS (Fig. 1). This growth banding is controlled by variable Fe, Mg and minor Zn content, which substitute for Mn in the wolframite structure. Therefore, a negative correlation between the GSV and Fe and Mg content has been observed (Fig. 1d) - an increase of Fe and Mg content from one to two orders of magnitude results in a decrease the GSV of up to 30% (Figs. 1b-c). Titanium (100's ppm level) positively correlates with the GSV.

IR microscopy of pyrite crystals associated with the studied wolframite revealed growth zoning, which has been investigated by EMP and is controlled by variable As and Co content, substituting for S and Fe respectively (Abraitis et al. 2004). Cobalt and arsenic content was often below LOD of the EMP, however in some of the dark growth bands (low GSV, ~ 20%) As concentration reaches 0.49 wt.%. Further LA-ICP-MS analyses will be processed to quantify the Co and As content variation in the pyrite.

IR microscopy revealed growth zoning in enargite from high-sulfidation epithermal veins (Kouzmanov et al. 2010), and has been investigated by EMP and LA-ICP-MS analyses. A clear negative correlation has been identified between the Fe and Sb concentrations and the GSV of the associated growth zones. High concentration of Fe and Sb, 160 and 10 000 ppm, respectively, are present in growth zones with 30% GSV, whereas lower concentration of Fe and Sb, 10 and 3000 ppm respectively, are present in growth zones with 80% GSV.

Image analysis of the GSV on transmitted visible and near IR light photomicrographs in combination with EMP and LA-ICP-MS allows first order estimation of the effect of minor and trace elements on the mineral transmittance, which is a crucial prerequisite for a successful fluid inclusion study. However, FTIR microspectroscopy measurements are required for quantitative analysis.

Aknowledgement

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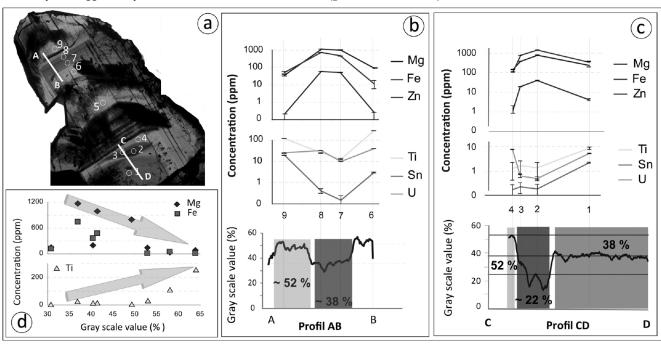


Figure 1. a) Transmitted-light photomicrograph of huebnerite with growth bands. Circles locate ablation pits from the LA-ICP-MS analyses and AB and CD lines correspond to profiles from 1b and 1c; b) Trace element content along profile AB and associated gray scale values; c) Trace element content along profile CD and associated gray scale values; d) Correlations between gray scale values of the huebnerite and trace element concentration.

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Main volcano-sedimentary Lithofacies at the Cretaceous Madneuli copper-gold polymetallic deposit, Lesser Caucasus, Georgia

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The Cretaceous Madneuli barite-gold-copper-polymetallic mine is the major ore deposit of the Georgian Bolnisi mining district. The Bolnisi volcanic-tectonic depression is part of the Artvin-Bolnisi Unit, which is characterized by an arc association formed mainly during the Liassic-Campanian interval. It is located between the southeastern Black Sea-Adjara-Trialeti Unit to the north and the Bayburt – Karabakh Unit to the south. It represents the northern part of the southern Transcaucasus and the central part of the Eastern Pontides. The main ore bodies that were defined in the open pit include: (1) copper-pyrite, (2) barite polymetallic and (3) gold-bearing quartzites, from the base upward. Four structural-morphological ore body types are recognized at the Madneuli deposit: vein, disseminated, breccia and massive stratiform.

Subdivision and characteristics of the host rock units are based on detailed studies of each existing level of the open pit. The different units are characterized by variations in composition and texture. Eight lithofacies were singled out in our study for the first time in the Madneuli deposit. Further detailed studies are in progress. Descriptions and interpretations of the eight principal facies are summarized in Table 1.

The high proportion of volcanic glass, which is common in subaqueous lavas, the abundant pumiceous ash and lapilli, the absence of subaeral lithic clasts, a relatively good hydraulic sorting, and various forms of bioturbation, which are systematically associated with wavy parallel, graded tuffs and with accretionary lapilli tuffs are evidence for marine, mostly shallow marine conditions of the depositional setting of the Madneuli host rocks. Such a setting suggests that the Madneuli deposit was mostly formed under subaqueous conditions, as is common for volcanogenic massive sulfide deposits, and contradicts some previous investigations suggesting mostly subaeral conditions during some of the Madneuli host rock and ore deposit formation. This conclusion is supported by recently discovered radiolarian-bearing horizons within the open pit. The study of which is under progress.

Table 1 - Summary of the main volcano-sedimentary lithofacies of the Madneuli deposit

Lithofacies	Characteristics	Interpretation
Rhyolite pyroclastic lava- flow with flow foliation	Presence of shards of felsic rocks along flow foliations. Porphyry structure with plagioclase, feldspar and quartz phenocryst. Groundmass is perlitic, amygdales are filled with quartz. Locally strongly silicified.	Coherent facies of domes (cryptodomes) or volcanic sills.
Columnar-jointed ignimbrite	The shapes of columnar jointed ignimbrite are rectangular. Groundmass is typically perlitic, with a spherulitic texture of the volcanic glass, with oval shaped quartz crystals. High temperature devitrification of volcanic glass.	Depositional setting below a storm-wave environment.
Fine-grained accretionary lapilli tuffs and tuffs with bioturbation	Massive or normally graded. Recrystallized volcanic glass in the groundmass. Lapilli of various sizes, oval shapes, filled with quartz. Lapilli- rim type, with a core of coarse-grained ash, surrounded by a rim of finer grained ash.	Shallow water sedimentation; in part water settled volcanic ash.

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Water-settled pyroclastic fall deposit	Inner flow stratification within a single layer shows fine-grained lamination, normal grading and lamination, thick units with clasts and reverse grading at the top and fine-grained pelitic in the upper part.	Resedimentation of shallow submarine pyroclastic flow; down-slope transport by high concentration turbidity currents.
Rhyodacitic intrusion	Massive. Evenly porphyritic groundmass micropoikilitic, rarely pumiceous.	Coherent facies of lavas or dome.
Non-stratified rhyolitic to dacitic breccias facies	Massive, poorly sorted, clast- to matrix-supported. The fragments of the rocks are slabby, irregular, blocky and oval shaped. Locally this unit is silicified and altered.	Autoclastic breccia from the margins of subaqueous lavas or cryptodomes.
Hyaloclastite	Carapace andesitic breccia flow. Hyaloclastite – with pillow like shapes and glass-like selvages. Groundmass with a perlitic structure. Fractures are defined by chlorite, and glass is replaced by quartz, feldspar, sericite and epidote.	Lobe hyaloclastite facies, reflects a continuous evolution of textures and structures that formed during extrusi- on in response to rapid chilling and quench fragmentation of lava by wa- ter or by wet hyaloclastite formed

Provenance of imported basaltic millstones in Switzerland during Roman times.

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In several areas of the Mediterranean, young vesicular lavas are croping out. From the Bronze Age, the excellent abrasive properties of this type of rocks were noticed and they were used as millstone for grinding cereals. With the development of waterpowered mills during the Roman period, the high quality of this material makes it valuable enough to be traded at long distances.

In Switzerland, Roman watermills have been excavated in Avenches VD, the ancient town Aventicum capital for the Helvetii, and in Rodersdorf SO, a large farming villa. The millstones were made of light grey vesicular lavas.

We investigate 34 samples by mineralogical and petrological techniques (XRD, XRF, microscopy). We can characterize 7 different lithologies, each being typical for a single quarry. They are different from the wellknown sources in Italy (Eugean Hills, Vulsini, Somma-Vesuvius, Vulture, Etna, Sardinia), in Southern France (Agde) and Germany (Eifel). Geochemical affinities point to the recent volcanism of the French Massif Central but it is still impossible to point exactly specific localities. For several decades, the production of millstones during the Roman times in the Central Massif has been postulated, but no quarry remains are located. Our data provide a new insight on the complexity of the production and trade of this material.

from previous lobes.

Isotope geochemistry of the Varuträsk pegmatite (northern Sweden)

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The Varuträsk pegmatite, located in the Skellefte district in northern Sweden, is a classical representative of LCT-type (petalite subtype) rare element pegmatites (Cerny 1991; Cerny & Ercit 2005). Detailed geochemical and isotopic studies of this well-documented pegmatite body can help to address important questions in pegmatite petrogenesis, such as the processes controlling internal evolution and zoning, and the potential role of an aqueous fluid phase in the evolutionary history. The Varuträsk pegmatite shows a typical differentiation pattern, composed of well-developed border, wall, intermediate and core zones (Quensel 1952). Late stage assemblages are characterized by replacement features that might relate to interaction with a highly evolved melt or an aqueous fluid phase. Previous work (Matalin 2010) has focused on the major and trace element characteristics of key minerals (feldspars, micas, tourmaline, columbite-tantalite), constraining progressive magmatic fractionation trends in the primary pegmatite zones. Significant compositional changes observed in the late-stage mineral assemblages (e.g., reversals of magmatic fractionation trends, depletion in elements typically enriched in aqueous fluids) indicate that most likely an aqueous fluid exsolved after the development of primary pegmatite zonation.

The present study has been carried out to further constrain the role of an aqueous fluid phase, and additionally attempts to trace the source of the parental granitic magma. Stable isotope analysis (O, H, B) has been performed on quartz, mica and tourmaline of all principal mineral assemblages in the pegmatite. Radiogenic isotope (Rb/Sr and Sm/Nd) data have been obtained from two granite suites (Skellefte- and Revsund-type granites; Claesson & Lundquist 1995) that are likely source candidates, host rock amphibolites as well as pegmatitic apatites and feldspar minerals. The δ^{18} O values are in the range of 9.7 to 14.0 ‰, and the resulting equilibrium temperatures for quartz-mica pairs are 550°C for the wall zone and 450°C for the intermediate zones. Hydrogen isotope analysis of micas yielded δ D values between -75.8 and -19.2 ‰. Both oxygen and hydrogen isotope data display an inward fractionation trend. Boron isotope data of tourmalines obtained using SIMS microanalysis are between -14.6 and -6.2 ‰. The δ^{11} B data of different tourmaline types conforming to the primary pegmatite zonation show a clear magmatic fractionation trend, whereas tourmalines related to late-stage assemblages show a reversed fractionation that is correlated with the trends shown by several major and minor elements in the tourmaline (Na, Fe, Mn, F). The radiogenic isotope data indicate an arc environment setting for the Revsund granitic suite, and a sedimentary (S-type granite) origin for the parental granite of the Varuträsk pegmatite which is most probably provided by the Skellefte type granites. This interpretation is supported by the elevated levels of phosphorus (London 2008) in the Varuträsk pegmatite, and the boron and oxygen isotope data that both point to an upper crustal S-type granitic origin.

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Main Features of the Tectonic Pattern of the Zangezour Ore District of Southern Armenia, Lesser Caucasus

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The Zangezour ore district is the southern segment of the Tsaghkounk-Zangezour structure metallogenic zone (Aslanyan 1958). It is located in the Lesser Caucasus of southern Armenian, generated during the collision of the southern margin of the Eurasian plate and the northern margin of the Arabian plate (Sosson et al. 2010).

The region is bounded by north-northwest oriented deep-seated tectonic zones: the Khustup-Giratakh fault in the east and the Ordubad-Salvard fault in the west. To the south, the folded and discontinuous structures are traced in the territory of Iran. The northern boundary with the Vayk synclinal block passes through the sub-latitudinal fractures of the upper parts of the Vorotan River.

The Khustup-Giratakh fault zone lies along the Shirak-Zangezour ophiolite zone. The Ordubad-Salvard fault zone, which delimits the blocks of Zangezour in the east and Nakhichevan in the west can be followed along the southern fragment of the Yerevan-Ordubad deep fracture zone (Aslanyan 1958). As the Zangezour block was uplifted, the Upper Eocene to Miocene sedimentation was concentrated in the Nakhichevan depression, to the west of the Ordubad-Salvard fault zone.

The Zangezour ore district is characterized by abundant Upper Eocene to Lower Miocene magmatism, which generated the composite Meghri-Ordubad pluton (covering an area of more than 1300 km², the largest pluton in Transcaucasia) and the Bargushat group of intrusions (Karamyan 1978; Melkonyan et al. 2008).

The large discontinuous intrablock faults, complicate the internal structure of the region, and consist of variably oriented extensive zones, among which the submeridional and sub-latitudinal ones are particularly remarkable (Tayan et al. 1976).

The central ore- and magma-controlling zone is located in the axial part of the Zangezour block, and is the product of a long and multi-stage evolution. It is manifested from the Lower Miocene by the formation of porphyritic granitoids prior to hydrothermal mineralization. This central zone is 10-12 km wide, which occupies a small area of the entire 60 km wide ore district.

The eastern border of the study zone in the southern part of the region is characterized by meridionally and submeridionally oriented fractures, which traced along the shores of the Meghri River and further to the north, and traced by dyke, rhyo-dacite, metasomatic rocks and the ore-bearing districts of Lernadzor, Pkhrout, Karmir-Kar, Tagamir, and Aygedzor (Eghnikasar district). The eastern Zangezour block was uplifted (Tayan et al. 1986), and resulted in the formation of the Meghri-Tey graben-synclinal structure within the limits of Central zone, the width of which is about 3,5-4 km. Its western limit is the Tashtoun fault. The formation of graben occurs essentially during the Mio-Pliocene accompanied by the deposition of terrigenous-fragmental lacustrine deposits of the Nor-Arevik Formation. It contains large fragments of ore-containing mid-Eocene volcano-sedimentary formations, which were derived from intrusions that are ore-containing in the Tey, and Terterasar gold-sulphide deposits. The formation of graben was favourable to preserve the economic copper-molybdenum and gold-sulphide deposits of the Meghri pluton from erosion.

In brief, three longitudinally oriented complex zones can be distinguished in the region, which were likely channel-ways for the circulation of hydrothermal solutions. They are the: 1. Giratakh; 2. Salvard-Ordubad and 3. Central- Zangezour zones.

The copper-molybdenum-porphyritic mineralization (Upper Eocene-Lower Miocene) conforming to the granite-granodiorite model (Melkonyan 1981), is the major one in the region. It was formed during complex geodynamic conditions and it consists of numerous ore prospects and deposits, among which the Kajaran deposit is the largest, with >2 milliards t. of ore.

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Fluid inclusion evidence for magmatic-metamorphic fluid interaction in the copper-gold Sultana deposit at Huelva, Spain

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The intrusion related copper-gold Sultana veinfield in Huelva (SW of Spain) formed 10 Ma after the Santa Olalla Plutonic Complex emplacement, during the Variscan orogeny which was dated at 341 Ma. The intrusion is hosted by volcanosedimentary rocks and black shales of Cambrian age that were affected by an intense aureole of contact metamorphism.

Combined techniques of scanning electron microscope cathodoluminescence imaging (SEM-CL), detailed fluid inclusion petrography, microthermometry, Raman analysis and laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS) in single inclusions are applied to reconstruct the physical and chemical evolution of the hydrothermal system in Sultana. The study suggests that a low saline (<4 to 15 wt % NaCl eq; avg of 5 wt % NaCl eq.), $\rm CO_2$ bearing (up to 10.4 mole %) and intermediate density fluid with high ore-metal concentration (> 537 $\rm \mu g/g$ Cu, >539 $\rm \mu g/g$ S) is equivalent to an initial fluid pulse that was exsolved from an underlying carbonaceous melt. When this fluid rose reaching hydrostatic conditions, phase separation occurred by condensation of minor brine (~ 40 wt % NaCl eq.) and a low saline vapor phase (~ 2.4 wt % NaCl eq.) at ~ 350 °C and 100 - 300 bar, the latest carrying most of the copper, gold and sulfur (335 \pm 123 $\rm \mu g/g$ Cu, 11.9 \pm 8.7 $\rm \mu g/g$ Au and 1384 lld- $\rm \mu g/g$ S) into the system.

Coinciding with the dissolution of an early generation of quartz (Q1) during cooling and phase separation, sulfides were precipitated into open spaces together with the precipitation of a late generation of quartz (Q2) (Figure 1). In fact, Cu concentration drops from 700 μ g/g to less than 0.1 μ g/g in late fluid inclusions without proportional decrease in other elements. Gold was deposited in later stages in fractures within the chalcopyrite, probably due to the excess of sulfur in the vapor phase which could transport gold after the precipitation of Cu.

The Sultana orebody shares characteristics with intrusion-related Cu-Au deposits, with deeper parts of porphyry deposits and with mesothermal orogenic gold deposits, allowing the possible interaction of magmatic and metamorphic fluid components. With this study, we support that fluids originated from deep magmatic sources with some possible interaction of metamorphic fluids rather than mixing with external fluids at the depositional site of the mineralization.

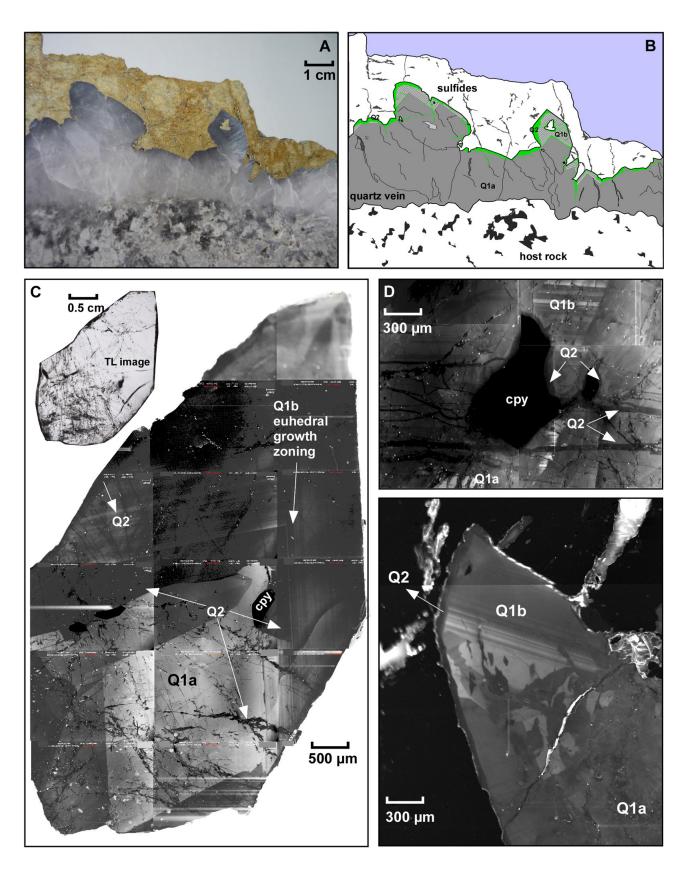


Figure 1. (A and B) Reconstruction of an area from the vein-sample CSU1 based on SEM-CL textures. Note that most of hydrothermal quartz vein infill is represented by the Q1 quartz generation, whereas Q2 forms a narrow rim of quartz around Q1 or fills fractures within Q1; (C) Photomosaic of a free standing quartz crystal (sample SUCH3) where the two quartz generations can be observed. This pattern can be observed in many samples where chalcopyrite and quartz formed in the center of the vein; (D) Detail of a small single grain of chalcopyrite that precipitated along a microfracture filled with quartz Q2 (sample CSU1A); (E) Thin rim of Q2 overgrowing euhedral Q1. The Q2 is always in direct contact with the main sulfide stage of chalcopyrite, bismutinite and gold-bearing minerals.

Dunite formation in the Lanzo peridotites, Italy: a morphological, petrological and geochemical study.

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The Lanzo ultramafic massif is located in the Western Alps, Northern Italy. This massif is formed by subcontinental mantle lithosphere peridotites and pyroxenites exhumed during Jurassic rifting related to the opening of the Piemont-Liguria ocean. During the early stages of exhumation this mantle portion underwent successive reactive and impregnating melt interaction phases. Intergranular porous melt percolation was first diffuse and then focused through high porous channels, which resulted in dunites bodies (Müntener and Piccardo, 2003). Dunites are clue for a better understanding of melt migration processes and evolution of mid-ocean ridge magmas and may develop during an advanced stage during the transition from a magma-poor margin to an (ultra)-slow spreading ridge. Here we present results from a morphological and geochemical study on olivine, spinel and clinopyroxene from Lanzo dunites.

Two distinct morphological and mineralogical types of dunite channels have been recognized. The first type is characterized by isolated straight and clinopyroxene-bearing dunite channels, with various and irregular size but especially as decametre-scale bodies. The second type is characterized by anastomosing networks of thin, braided clinopyroxene-free dunite channels. Olivine compositions are identical in both types in terms of Mg# (89.9 – 92.5) and trace element contents, while spinel compositions vary between the two types (TiO_2 : 730 – 3230 ppm and even higher for the second type, Cr#: 29.3 – 44.2).

In clinopyroxene-bearing dunites, two clinopyroxene shapes have been identified: cumulate grainal grains and typical interstitial grains. Granular grains are chemically homogeneous over the entire grain, while interstitial grains show incompatible trace element enrichment, including Na and Ti, and especially in Zr and Hf and a clear Zr/Hf ratio increase from core to rim of the grains. In addition, phlogopite and Ti-amphibole inclusions in dunite spinel surrounding small gabbroic dikes are enriched in incompatible elements, with positive Zr, Hf anomalies. Clinopyroxene chemistry and modal amounts may be related to conditions and time of the melt migration and allow us to establish a relative chronology of the dunite channel activity. Chondrite-normalized REE abundances of liquids in equilibrium with clinopyroxene have been calculated. The melt composition remains N-MORB type during the entire intergranular porous flow migration episode until the compaction event. At this point the melt composition seems to change and REE pattern of melt in equilibrium with interstitial clinopyroxene show a LREE enriched composition similar to E-MORB with a Zr and Hf positive anomaly.

The morphological and geochemical features can be related to two distinct crystallization regimes. The homogeneous granular grains crystallized in equilibrium from the cooling migrating melt; while the interstitial grains are the result of crystallization of interstitial trapped melt, probably induced by compaction and porosity decrease of the peridotites, during the final stages of melt migration. These last increments of melts probably represent refractory initial compositions that fractionate in the mantle forming metasomatic assemblages.

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The coupling of deformation and reaction kinetics in the case of positive volume change reactions

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Common petrologic grids derived either by experimental or theoretical investigations do not consider the role of deformation during metamorphism. Moreover, rheological studies rarely take in the account mineral reactions in the system. In natural rocks, however, deformation and reaction are coupled. The majority of reactions in nature involve volume change. In some reactions volume change reaches almost 20% as for the transformation from jadeite to albite + quartz. Volume change causes reaction-induced stress. A number of studies have shown evidences for the existence of high transformation stresses in the materials as a consequence of the phase changes processes. The transformation-induced stresses initially produce elastic strain. Afterwards, if the reaction volume change is large enough than either plastic or viscous deformation occur.

In our previous studies we performed experiments on partial melting of quartz-muscovite system that has 3 % of positive volume change. It has been showed that deformation enhances reaction kinetics and during shear deformation melting rate is 1.7 times faster than at hydrostatic conditions. To explain this fact we considered few different hypotheses as shear heating, strain energy, surface energy, local pressure drops and effective viscosity. Our results suggest that the reduction in effective viscosity induced by macroscopic shear can have a profound effect on reactions that have a non-zero isobaric volume change. In contrast, all other explanations of increased melting as shear heating, strain and surface energies and local pressure drops effects are eliminated by our first order considerations. To verify the significance of effective viscosity effect we performed a model of the spherical liquid inclusion growth within an inert solid matrix. In this model thermodynamics of melting reaction and mechanical response of solid phase are coupled.

In this study we also propose a general version of the model of deformation and volume positive reaction coupling, expanding its relevance to many problems that exist in the current studies. For example, occurrence of highly deformed minerals in the contact with undeformed ones (Lenze et al. 2005) or kinetics of rim growth between quartz and olivine depending of geometrical relationships (Schmid et al. 2009).

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Geological Setting of the Drmbon Copper-Gold Deposit, Nagorno Karabakh Republic, Lesser Caucasus

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The Drmbon copper-gold deposit is located in the Mekhmana ore district (Nagorno Karabakh), which is the part of the Jurassic-Cretaceous Pont-Somkheti-Karabakh-Elburs island arc system of the Lesser Caucasus. The deposit was discovered in 1933. Recent mining of deposit, with mainly underground working, enabled us to clarify several important facts about the geological setting of the Drmbon deposit.

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The Drmbon orefield occurs in a caldera setting of 4km in diameter. The lower volcanogenic suite of the Drmbon volcanic sequence consists of Lower Bajocian basaltic andesites, andesites and Upper Bajocian andesites, dacites and tuffs. The upper volcanogenic suite is composed of Bathonian basaltic andesites, andesites and their tuffs and volcano-sedimentary rocks. In addition, there are also Upper Jurassic volcanic agglomerates (basaltic andesite – andesite) and volcano-sedimentary rocks. There are abundant outcrops of subvolcanic rocks and dikes of different composition ranging from basaltic andesite to rhyolite, as well as felsic extrusions. Some of the subvolcanic rocks and dikes are located in arcual structures. In the northeastern part of the caldera there is a large outcrop of an Upper Jurassic stratiform diorite body.

In the northeastern part of the caldera, the rock sequences preserved their periclinal bedding. By contrast, in the south-western part of caldera, the primary periclinal bedding of the rock sequences was modified and were inclined to the center of the caldera during subsidence. As a result of these movements, a domelike structure was formed in the south-western peripheral part of the caldera, which was favorable for ore formation. The Drmbon deposit is located at the intersection of the caldera boundary and a northwest-striking fault.

The major rocks units in the ore deposit area are lower volcanogenic sequence (Lower and Upper Bajocian lavas and tuffs), Upper Bathonian subvolcanic quartz dacites and Upper Jurassic (Oxfordian) agglomerates. The main host rocks of the deposit are Upper Bajocian andesites and dacites, which were mainly brecciated during caldera formation. The thickness of the Upper Bajocian rocks in the deposit is between 50 and 65m.

An important role during ore deposit formation was played by subvolcanic (sill form) quartz dacites and a shear zone at the contact between the quartz dacites and the underlying host rocks, which stopped the main part of the hydrothermal fluids. As a result of this, massive ore zones are now located below the quartz dacites along their contacts. Quartz dacites were injected between the lower and the upper volcanogenic suites, parallel to the subsidence of the volcanic edifice. As a result of irregular movments of viscous magma along interlayer areas, quartz dacites acquired an ataxitic, fluidal and breccia texture. The Thickness of the quartz dacite sill in the deposit reaches 200m.

Quartz dacites in the deposit crosscut Bathonian volcanic rocks and are crosscut by dike-form and vent bodies of agglomerates. On the southeastern flank of the deposit, agglomerates occur as beds, which in fill out and smooth out the irregularities of the paleorelief. Clasts in agglomerates are generally rounded, locally nearly isometric in size from 3-4cm to 1-2m, the percentage of which varies between 40 and 70%. Agglomerates show no sorting of clasts. Clasts consist predominantly of andesites and basaltic andesites, and subsidary compact, fresh dacites. Agglomerates also include large blocks (10-20m) of early Oxfordian limestone.

Dikes in the Drmbon deposit consist of two varieties: dacites and andesites, which are mostly located in arcual faults and have a 55-75° dip toward the center of the caldera. They crosscut all volcanogenic rocks in the deposit. All dikes in the deposit are altered, but they do not contain any mineralization. Numerous observations in the mines and also studies of thin sections, collected from the contact of the dikes with the ore bodies, show evidence that the dikes pre-date ore formation.

In the deposit, there are abundant bodies of explosive-injection breccias. These rocks post-date the dikes, but pre-date or are coeval with mineralization. In the mine, there are explosive-injection breccias with numerous rounded fragments of plagiogranite, outcrops of which remain unknown in the whole ore district. A fragment of plagiogranite was also found in agglomerates. This suggests that there is a plagiogranite intrusion at depth below the Drmbon deposit.

The Drmbon deposit consists three main lens-form ore bodies. Their thickness varies between 20m and 80m. As a rule, the upper boundaries of the ore layers are clearly exposed and are characterized by a shear zone, at the contact of subvolcanic quartz dacites with underlying ore-bearing rocks. The richest massive sulfide ore lenses (2-6m of thickness) are located immediately below the shear zone. The lower parts of the ore bodies pass gradually into a zone of disseminated sulfide mineralization and into quartz - carbonate – sericite altered host rocks with pyrite dissemination.

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When did the large meteorite shower Jiddat al Harasis 091 arrive on Earth?

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Jiddat al Harasis (JaH) 091 is a large meteorite strewn field in the desert of Oman (Russel et al. 2004, Gnos et al. 2006). About 670 fragments (different find places of paired samples, some of them are further fragmented) with a total mass of ~4 metric tons were so far recognized to belong to the same fall event. They are distributed over an ellipse of 51.2 km by 7.2 km. Some of the largest fragments formed a breccia that is composed of meteoritic fragments, iron hydroxides, a weathering product of the meteorite, and soil particles.

Terrestrial ages, the residence time of meteorites on Earth, are usually determined using the decay of spallation-produced radioactive isotopes such as ²⁶Al, ³⁶Cl (for meteorites with long terrestrial residence times, Antarctica) or ¹⁴C (shorter time scale, hot deserts) (e.g Jull 2006). A limiting factor of radiocarbon dating is the size of the preatmospheric meteoroid since the production of cosmogenic ¹⁴C is restricted due to shielding. Such ages can be corrected with ¹⁰Be.

Beside this standard method we tried to estimate the terrestrial age of JaH 091 with several other indirect approaches: A well-known feature of meteorites recovered from hot deserts is the continuous accumulation of Sr and Ba (e.g. Al-Kathiri et al. 2005). By measuring natural and cut surfaces with handheld X-ray fluorescence (HHXRF), the degree of contamination can be evaluated. Another parameter is the degree of alteration of the primary minerals observed in thin section using reflected light (Wlotzka 1993). And finally, the presence of water soluble salts is an indicator of terrestrial alteration.

Since the degree of contamination with salts is size dependent and influenced by local soil composition, this parameter is not useful to determine the terrestrial age. The Sr and Ba accumulation is also a result of local soil composition, but seems to be more robust, since soil composition in Oman is relatively homogeneous. The degree of oxidation as represented by the weathering degree correlates with terrestrial age but can be inhomogeneous in a sample and is usually lower in large samples.

The find site of the largest fragments of the JaH 091 strewn field offered us the possibility to test a new approach: Some large meteorite pieces were completely buried into the soil. We took two soil samples direct under a large meteorite fragment from the main impact site and dated its last exposure to the sunlight, which is believed to be close to the terrestrial age of the meteorite, by optical stimulated luminescence (OSL). First results show a good agreement between the radiocarbon (19.3 \pm 1.3 ka) and the OSL (15.2 \pm 1.4 and 18.6 \pm 1.5 ka) ages. The mean weathering grade of JaH 091 is W3, which is also in the range of ¹⁴C terrestrial ages of 15 - 20 ka from meteorites found in Oman. In addition, the amount of Sr and Ba contamination on exposed surfaces (~160 ppm and ~ 90 ppm, respectively) also fits this age range.

In conclusion, we can say that the terrestrial age of JaH 091 is between 15 and 20 ka and that the stones of this shower have undergone several kinds of alteration and contamination.

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